The Role of Calcium in Geopolymerisation

by

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Department of Chemical and Biomolecular Engineering
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Australia
To Mum

For her unconditional love that gives me a meaningful life.

&

To My Auntie Grace

For her love and devotion towards me.
Those who can truly be accounted brave are those who best know the meaning of what is sweet in life and what is terrible, and then go out undeterred, to meet what is to come...

*Pericles*
Abstract

The search for a new environmentally friendly construction material that will match the durability of ancient concrete has stimulated interest in geopolymerisation in recent times. Despite extensive research that has been conducted on various aspects of geopolymerisation, especially in enhancing the properties of resultant binders and understanding the chemical mechanisms involved, a number of questions remain to be answered. The role of calcium in geopolymerisation is one of them. It is known that the presence of a moderate amount of calcium in a geopolymeric binder will improve the resultant compressive strength. However, it is still unclear whether calcium will play a charge-balancing role within the aluminosilicate structure (to maintain electroneutrality in a similar way as alkali metal cations, Na\(^+\) or K\(^+\), or perhaps an alternative role. In addition, the role of calcium in geopolymerisation is of great interest because it is proposed for the first time that calcium links geopolymer chemistry to, and distinguishes it from, ordinary Portland cement (OPC).

In the thesis various types of calcium materials (including an industrial waste - granulated blast furnace slag, GGBFS) having different elemental compositions and mineralogies are added to a calcium-free metakaolin (MK)-based geopolymeric system, in order to study the role of calcium in geopolymerisation. The results have confirmed that moderate addition (up to 20 mass\%) of calcium sources will increase the resultant compressive strength of the binder; however the role of calcium in each case is found to be different. In general, the role of calcium in geopolymerisation is dependent on (1) the type and nature of calcium material used, (2) the alkalinity of the alkaline activator and (3) the mass ratio between different raw materials used in the synthesis. These factors all affect the concentration of “free” soluble species (most importantly silicate, aluminate and calcium) present in the alkaline medium, which will further determine the subsequent reactions taking place and ultimately the role of calcium in geopolymerisation.
For the first time, a calcium silicate hydrate (CSH) gel, which is a major binding phase in OPC, is found to form simultaneously with a geopolymeric phase at specific conditions. Binders consisting of both these two phases are generally found to have better compressive strength and this includes binders synthesised from an alkaline activated MK-GGBFS system. A comprehensive study of the MK-GGBFS system has demonstrated that an industrial waste, such as GGBFS, can be utilised to provide additional benefits (e.g. better compressive strength and durability) in the production of a novel construction material. The results from the MK-GGBFS system alone are of great environmental and commercial value.

The CSH phase formed simultaneously with the geopolymer phase is found to have a significantly lower Ca/Si ratio than the CSH commonly formed by the hydration of ordinary Portland cement, while the geopolymeric gel formed is found to have similar aluminosilicate structure as that of previous research. It is suggested in the thesis that voids and pores within the geopolymeric binder become filled with the CSH gel, which helps to bridge the gap between the different hydrated phases and unreacted particles. The result is an increase in mechanical strength with time, similar to ancient concrete, which is renowned for its durability.

The coexistence of both geopolymer and CSH gels exists at specific conditions and it often takes place when a low concentration of NaOH and a calcium source that can readily dissociate its calcium species into the solution phase (e.g. GGBFS and calcium sulphate hemihydrate) is used. Calcium dissolved from a calcium source will react with soluble silicate or aluminate species to form CSH or calcium aluminate hydrate in preference to the formation of geopolymers with calcium playing a charge-balancing role. In cases where calcium sources have limited solubility in alkaline condition (e.g. wollastonite and calcite), the chemical role of these materials in geopolymerisation is only minor. Subsequently, a comparatively low early compressive strength (<20MPa at 28 days) is exhibited by these binders. In contrast, the compressive strength of these binders is found to improve significantly with time by playing a predominant role as a physical filler/micro-aggregate in reinforcing the physical structure.
The geopolymeric structure is found to be the dominant phase formed with a scattering of small calcium precipitates situated in the binder at high alkalinity, with calcium playing a lesser role in affecting the nature of the end product. The coexistence of the two phases is not observed at high alkalinity unless a significant amount of "free" soluble calcium species is present initially. This may be achieved by using a calcium material that is highly soluble at high alkalinity (e.g. calcium sulphate hemihydrate) or by adding the calcium material in a substantial amount. A chemical mechanism has been proposed in the thesis on how the presence of calcium source in the alkaline activation of MK could result in the formation of two separate phases - geopolymers and calcium silicate hydrate.

A chelating agent, Ethylenediaminetetraacetic acid (EDTA), is also used to understand the role of calcium in geopolymerisation, especially in its influence on the dissolution process. It is found that the dissolution rate of calcium from various calcium sources is strongly dependent on the amount of EDTA present, and that the dissolution rate increases with increasing concentration of EDTA. The rapid increase in the concentration of soluble Ca species appears to promote the formation of precipitates with a higher concentration of calcium and silicon in a highly alkaline environment to some extent. However the nucleation growth of calcium silicate hydrate (CSH) gel along with a geopolymeric phase is not promoted and observed, because a large proportion of dissociated Ca species rather form metal complexes with EDTA instantaneously. This has confirmed the proposed chemical mechanism that the formation of both geopolymer and CSH phases would only be promoted in the presence of a high concentration of "free" (i.e. no complexed) soluble Ca species. The thesis makes a significant contribution to the mechanistic understanding of geopolymerisation. It has provided the fundamental stepping stone for further research in years to come.
Preface

I hereby declare that, to the best of my knowledge, this thesis is original in its entirety and contains no material which has been previously published by another person, except where due reference is stated. In addition, no part of this work has been submitted for the award of any other degree or diploma in any university.

I certify that the work has been undertaken solely by the candidate, except where due acknowledgement is given. The text of this thesis, exclusive of tables, figures and bibliography, does not exceed 100,000 words.

Christina Ka-Bik Yip

March 2004.
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Conference Presentations and Papers Published

A. JOURNAL PUBLICATIONS:


B. REFEREED CONFERENCE PUBLICATIONS:


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Chapter 1

Introduction

Geopolymers are a new generation of materials with diverse applications in the building industry and waste management. Geopolymers, which are sometimes referred to as alkali-activated aluminosilicate binders, represent a new group of cement-like materials that can be formed by mixing aluminosilicate materials (such as metakaolin or "kandoxi" and fly ash) with a solution of alkali or alkaline salts. The display of excellent mechanical property, fire, acid, corrosion and freeze-thaw resistance, low shrinkage, hard but smooth surface, thermal stability and precise moldability have made geopolymers a potential replacement for traditional ordinary Portland cement (OPC) in the future (Davidovits, 1991, 1994).

Geopolymerisation involves a chemical reaction between various aluminosilicate oxides ($\text{Al}^{3+}$ in IV-V fold coordination) with silicates under highly alkaline conditions. Due to the coordination of Al, other cations such as $\text{K}^+$, $\text{Na}^+$ and $\text{Ca}^{2+}$ must be present in the structure to maintain neutrality. Although the role of alkaline metals in geopolymerisation has been discussed extensively in the literature, the role of calcium in geopolymerisation has not been studied in any great depth. Recent research has only indicated that the presence of a small amount of calcium species in the system increases the compressive strength of the resultant binder, however, the exact role of calcium in geopolymerisation is still inconclusive.

A study into the role of calcium in geopolymerisation is not possible without a thorough understanding of cement chemistry. It is believed that calcium will play a significant role in linking the chemistries between geopolymers, OPC and alkali-activated cementitious systems. Moreover, in order to promote geopolymers as a suitable alternative to OPC, it is important to determine the technical advantages of geopolymers over Portland cement. It is also essential to relate geopolymers and OPC
chemically and structurally. Chapter 2 therefore presents a comprehensive introduction to the development and application of geopolymer and cement technology to the present day. Emphasis is placed on the fundamental chemistry involved in geopolymerisation and in the formation of calcium silicate hydrate (CSH, the major binding phase in OPC and alkali-activated cement). Chapter 3 provides a summary of the research methods, experimental methods and analytical techniques used throughout the thesis. Due to the lack of microscopic work conducted in the study of geopolymerisation so far, electron microscopy will be used extensively in the thesis. For the first time, the use of electron microscopy will allow the microstructure of geopolymers to be probed in detail.

The main objective of this thesis is to study and understand the effects of calcium addition (using different calcium sources) to geopolymers. Chapter 4 investigates the effect of ground granulated blast furnace slag (GGBFS) addition on a calcium-free metakaolin (MK) - based geopolymeric binder. GGBFS is essentially an amorphous source of calcium silicate material and it is used as the primary calcium source of interest throughout the thesis. GGBFS is a major industrial waste, and its successful application in geopolymer technology will be of significant commercial interest. The published literature on the utilisation of GGBFS in OPC and alkali-activated slag cement is considerable; therefore the results generated in Chapter 4 are of further interest academically.

In an OPC system, the CSH phase will form when soluble calcium and silicate species are present in a neutral to mild pH environment. It is proposed that provided sufficient calcium is added to a geopolymeric system, a CSH based cementitious material may also result. Further microanalysis of the MK-GGBFS binder presented in Chapter 5 will demonstrate that it is indeed possible to have both geopolymeric and CSH gels forming simultaneously in a single binder. A chemical mechanism of the alkaline activation of MK in the presence of GGBFS, and the mechanistic understanding of the coexistence of both geopolymeric and CSH gels are also presented in Chapter 5.

Chapters 4 and 5 study the effect of GGBFS in detail and the chemical mechanism proposed for the role of calcium in geopolymerisation is also based on the MK-
GGBFS system. The applicability of the proposed mechanism to other calcium silicate sources remains unclear. Moreover, it is still uncertain whether it is possible to formulate a geopolymeric binder with calcium playing a charge-balancing role (similar to that of Na$^+$ or K$^+$), by the addition of a calcium silicate material to an alkaline activated MK binder. Chapter 6 therefore compares the effect of GGBFS to various other calcium silicate materials with different elemental composition and mineralogy on a MK-based geopolymeric binder. The correlation between the solubility of calcium species from each source material in an alkaline environment and its possible participation in the formation of the CSH phase will be discussed in Chapter 6.

The calcium materials investigated so far are limited to calcium silicate materials, in which no substantial amount of anions, other than silicate and hydroxide, are present in the system. Chapters 7 and 8 investigate the role of calcium materials containing anions such as sulphate (calcium sulphate hemihydrate) and carbonate (calcite and dolomite) in geopolymerisation.

Chapters 4 to 8 examine the effect of different calcium sources (calcium silicate, calcium sulphate and calcium carbonate) in geopolymerisation. Calcium is found to play a prominent role in affecting the reactions taking place in the alkaline activation of metakaolin. Dissolved calcium species present in the system are suggested to initiate the nucleation growth of calcium silicate hydrate (CSH) gel simultaneously with a geopolymeric binder following the chemical mechanism as proposed in Chapter 5. In valuing the importance of the initial concentration of soluble calcium species present during alkaline activation, a calcium chelating agent, ethylenediaminetetraacetic acid (EDTA), is used in Chapter 9. This work examines the effect of EDTA on the dissolution of Ca, and to a lesser extent on Al and Si, from source materials and its impact on the subsequent reactions in the alkaline activated system. The importance of calcium in controlling the reactions taking place in a geopolymeric system at the early stage, and its significance in determining the structure of geopolymeric products are demonstrated.

The results presented in each of Chapters 4 to 9 are based on recently published manuscripts. Therefore, most chapters contained in this thesis are written in a stand-
alone fashion in addressing an individual topic. Chapter 10 therefore concludes and integrates the ideas and major findings presented in this thesis in a coherent conceptual model.
Chapter 2

The Chemistry of Cement and Geopolymerisation

This chapter presents a comprehensive introduction to the development and application of geopolymer and cement technology to the present day. The current environmental challenge facing the cement industry will also be detailed.

The focus of the thesis is to understand the role of calcium in geopolymerisation. This study is not possible without a thorough review of cement chemistry, because it is believed that calcium will play a significant role in linking the chemistries between geopolymers, ordinary Portland cement (OPC) and alkaline activated cementitious systems. The main objective of this chapter is to present a literature review covering the fundamentals of OPC, alkaline activated cement, and geopolymer technology. Some of the aspects presented in this chapter will be discussed further in subsequent chapters.

2.1 Construction Industry

2.1.1 Overview

Concrete is one of the most commonly used man-made composites in the construction industry. It is composed mainly of three components: cement, water and aggregate, and sometimes with an additional material, known as an admixture, in order to modify certain properties of the resultant matrix (Jackson and Dhir, 1996). As the binding agents in concrete and mortars, hydraulic cements (a powder material that reacts with water to produce a physically strong as well as chemically insoluble precipitate) are key construction materials. Cement is the chemically active constituent, but its reactivity is only brought into effect upon mixing water. The aggregate plays no part in chemical reactions, but acts as a filling material with good resistance to volume change, which generally takes place within the matrix after the mixing. The study
into the actual cement used in binding the concrete is the main focus of current cement research. A more complete review of concrete technology can be found in the works by Neville and Brooks (1990), Jackson and Dhir (1996), and Gani (1997).

Amongst all commercially available hydraulic cements, Portland cement is the most widely used. It was developed in 1824 by Joseph Aspdin and derives its name from Portland limestone in Dorset because of its close resemblance to this rock after hydration has taken place (Jackson and Dhir, 1996). Twenty years later in 1844, Isaac Johnson discovered the modern high-temperature process for manufacturing Portland cement (Gani, 1997).

From the statistics conducted and complied by the U.S. geological survey (USGS), the global production of hydraulic cement was 1.6, 1.66 and 1.7 billion metric tons for three consecutive years starting from 1999. As shown in Table 2.1, China, India and United States are the top 3 producers of hydraulic cement in the world. Australia is not one of the top cement producing nations in terms of volume, however, there is still approximately 7.5 million metric tons of hydraulic cement being produced annually since 2000. There are 6 main cement producers in Australia as shown in Table 2.2; they represent approximately 76% of the total cement production in Australia.

Despite the environmental concern over the cement industry (as discussed in Section 2.2.1), the demand for this construction material will remain strong in this century, especially in the developing countries in the eastern part of Asia. In 2000, Asia accounted for about 59% of the world total production of hydraulic cement (van Oss, 2001). In China alone, the output has increased by 107 million metric ton annually since 1995 (van Oss, 2001).

Although Australia is considered to be a relatively small player in the Asian-Pacific cement industry, it has an abundance of natural resources, and mineral and mining industries. Australia therefore has the potential to increase its share in the cement market. This is especially true in the area of “high-tech environmentally friendly” cement, such as geopolymers, which have the potential to unload some of the environmental burdens experienced by the cement industry today. Moreover, a number of mineral or industrial wastes including granulated blast furnace slag from
the iron and steel industry can be readily utilised and incorporated in large quantities in the manufacture of geopolymers. This is of importance because, Australia currently accounts for more than 15% of world production in iron and steel (Lyday, 2001).

2.2 Ordinary Portland Cement (OPC)

2.2.1 Environmental Issues

Current cement production involves extensive mining and manufacturing operations. Most mine and quarries supplying the cement industry are open pit operations. Environmental issues affecting the mining of cement raw materials are common to most surface mines. These include: potential problems with dust, increased sediment loads to local streams, noise, and ground vibrations from blasting. The manufacture of cement itself represents a greater environmental concern. A large quantity of carbon dioxide (CO₂, a greenhouse gas) is generated through the fuel combustion and calcination of carbonate in the clinker kiln. The calcination process essentially follows Equation 2.1:

\[ \Delta \]

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \] (2.1)

Approximately 1 ton of CO₂ is released per ton of ordinary Portland cement (OPC) produced (van Oss, 2001). Based on the statistics as shown in Tables 2.1 and 2.2, approximately 1.7 billion ton of CO₂ was released in the Year 2001 through cement production alone. The cement industry remains one of the largest industrial sources of CO₂ and is perhaps the single largest industrial source (or possibly second to the iron and steel industry) of CO₂ not derived from the combustion of fuels (van Oss, 2001). Moreover, the manufacture of OPC involves the grinding of raw materials, the calcination of raw materials at 1500°C and the grinding of cement clinker and gypsum. It is an energy-intensive process and requires approximately 4000MJ/tonne of cement produced (Shi and Qian, 2000).

The cement industry is under increasing pressure to reduce the emission of CO₂ and other pollutants. It is therefore essential for cement manufacturers to consider all options in modifying the existing technique to increase efficiency, otherwise an
alternative environmentally friendly construction material has to be sought and developed. The former option requires an in-depth understanding of the process and chemistry involved in current cement technology.

2.2.2 Manufacturing of Ordinary Portland Cement

Portland cement is made up mostly of calcium silicate and is manufactured by controlled high-temperature burning in a kiln of a measured blend of calcareous rocks (usually limestone or chalk) and, as needed, lesser quantities of siliceous, aluminous, and ferrous materials found in argillaceous rock such as clay and shale (Gani, 1997; Jackson and Dhir, 1996). Table 2.3 shows a typical oxide composition of a Portland cement and Figure 2.1 shows a schematic view of cement production.

The solid raw materials are crushed and mixed in ball mills, and then heated in a kiln to about 1500°C to produce a clinker. The clinker consists of a number of compounds, which set or harden when the clinker is ground to a fine powder (cement) and then mixed with water (Gani, 1997). Since the clinker is formed by the diffusion between solid particles, intimate mixing of the ingredients is essential if a uniform cement is to be produced. This mixing may be in a dry or wet state depending on the hardness of the available rock.

The wet process is generally used for the softer materials such as chalk or clay. Water is added to the chalk and clay to produce a slurry which is eventually led off to a kiln. The dry process is used for harder rocks such as limestone and shale. The constituent materials are crushed into powder form with a minimum amount of water before feeding into a kiln. The manufacturing process for both dry and wet methods thereafter is similar with the dry process having a much shorter kiln in length. In general, the dry process is more energy efficient than the wet process. Once the clinker is cooled, it is ground in a ball mill to a powder with the addition of hydrated calcium sulphate (gypsum, calcium sulphate dihydrate, CaSO4.2H2O) to produce cement. The completeness of reactions which take place in the kiln is dependent on the mixing and particle size of the reactants (Gani, 1997).

Different types of Portland cement are obtained by varying the proportions of the raw materials, the temperature of burning and the fineness of grinding, and in some cases
by intergrinding the clinker with other materials such as flyash, ground granulated blast furnace slag and condensed silica fume. Certain additives may also be introduced for producing special cements, for example, calcium chloride is added in the manufacture of extra-rapid-hardening cement.

An OPC system can often be viewed as a quaternary system with four oxide components, CaO (C), SiO$_2$ (S), Al$_2$O$_3$ (A) and Fe$_2$O$_3$ (F). Table 2.3 highlights the oxide composition and origin of each component for each phase. OPC can also be viewed as a quaternary system based on four mineralogical phases: alite (tricalcium silicate - C$_3$S), belite (dicalcium silicate - C$_2$S), tricalcium aluminate (C$_3$A), and calcium aluminoferrite (C$_4$AF). Table 2.4 shows a typical composition of the resultant clinker. C$_3$S and C$_2$S are the most important components in the cement clinker, as they are responsible for most of the physical properties of the cement as discussed in the next section.

2.2.3 Hydration of Ordinary Portland Cement

The hydration reactions taking place when the OPC powder is mixed with water are complex and interdependent due to the multiphase nature of the cement clinker. The setting and hardening of the cement take place through a series of exothermic hydration reactions based on the four main phases (C$_3$S, C$_2$S, C$_3$A and C$_4$AF) in the system as shown in Table 2.4.

The two silicates, C$_3$S and C$_2$S, contribute most to the physical properties of hydrated hydraulic cement with C$_3$S being the most important constituent of Portland cement because it controls the normal setting and early strength development in OPC. When cement is mixed with water, the C$_3$S and C$_2$S phases will react and form crystalline calcium hydroxide (CH) and a calcium silicate hydrate (CSH) gel (CaO-SiO$_2$). Initially long needles of CSH are formed, which bond the cement particles together. Later, smaller needles of calcium silicate hydrate fill the remaining voids. The calcium silicate hydrate formed in the OPC system is normally non-stoichiometric and is often microcrystalline or amorphous. It is generally believed that CSH is the major binding phase in the OPC (Gani, 1997; Jackson and Dhir, 1996; Taylor, 1964). The overall reaction can be represented by Equations 2.2 and 2.3. Table 2.5 summarises the major hydration sequence of C$_3$S.
\[2\text{C}_3\text{S} + 7\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_4 (\text{CSH}) + 3\text{CH}\] for \text{C}_3\text{S} \quad (2.2)

\[2\text{C}_2\text{S} + 5\text{H} \rightarrow \text{C}_3\text{S}_2\text{H}_4 (\text{CSH}) + \text{CH}\] for \text{C}_2\text{S} \quad (2.3)

It should also be noted that upon contact with water, any free CaO (C, calcium oxide) in cement will readily hydrate to form calcium hydroxide. It is commonly acknowledged that the formation of calcium hydroxide makes the cement system alkaline to approximately pH = 12.5 (Gani, 1997).

The major difference between the hydration processes of the two silicates is the reaction time. \text{C}_2\text{S} hydrates more slowly and is mainly responsible for the strength development after 7 days, in contrast, the hydration process of \text{C}_3\text{S} is very rapid and is the main contributor to the early strength development (Gani, 1997; Jackson and Dhir, 1996; Taylor, 1964). It is generally believed that cement rich in \text{C}_2\text{S} results in a product with a greater resistance to chemical attack and a smaller drying shrinkage than other Portland cements (Jackson and Dhir, 1996). This is probably due to the lower production of calcium hydroxide with \text{C}_2\text{S} (Equation 2.3), in comparison to \text{C}_3\text{S} (Equation 2.2) for the equal amount of mole, which makes them less likely to be attacked by other chemicals, especially acid.

The hydration of \text{C}_3\text{A} can proceed with or without the presence of gypsum (CaSO\textsubscript{4}.2H\textsubscript{2}O). In the presence of gypsum, the \text{C}_3\text{A} and gypsum dissolve and react together to form ettringite (AFt, 6CaO.Al\textsubscript{2}O\textsubscript{3}.SO\textsubscript{3}.32H\textsubscript{2}O) as shown in Equation (2.4) with $S = \text{SO}_3$ and $H = \text{H}_2\text{O}$:

\[\text{C}_3\text{A} + 3\text{CSH}_2 (\text{gypsum}) + 26\text{H} \rightarrow \text{C}_6\text{AS}_3\text{H}_{32} \text{ (ettringite)}\] (2.4)

The ettringite will further react with the \text{C}_3\text{A} to form the more stable calcium sulphaaluminate hydrate (AFm, calcium monosulphaaluminate hydrate, 4CaO.Al\textsubscript{2}O\textsubscript{3}.SO\textsubscript{3}.12H\textsubscript{2}O) as shown in Equation 2.5:

\[\text{C}_6\text{AS}_3\text{H}_{32} + \text{C}_3\text{A} + 4\text{H} \rightarrow 3\text{C}_4\text{ASH}_{12} \text{ (monosulphaaluminate hydrate)}\] (2.5)
Ettringite crystals on the surface of cement particles are so fine that they cannot bridge the voids between the cement particles, and therefore do not form a solid structure, which leads to a delay in the setting time (Buchel et al., 2000).

In the absence of gypsum, the C₃A immediately reacts with water to form calcium aluminate hydrate, which fills the voids between the cement particles with its large crystals and leads to rapid solidification (Buchel et al., 2000). Equations 2.6 to 2.8 summarise the hydration process of C₃A in an OPC system in the absence of gypsum.

\[
\text{C}_3\text{A} + \text{CH} + 18\text{H} \rightarrow \text{C}_4\text{AH}_{19} \text{ (calcium aluminate hydrate)} \tag{2.6}
\]

\[
\text{C}_3\text{A} + 21\text{H} \rightarrow \text{C}_4\text{AH}_8 \text{ (hexagonal hydrate)} \tag{2.7}
\]

\[
\text{C}_4\text{AH}_{13} + \text{C}_2\text{AH}_8 \rightarrow 9\text{H} + 2\text{C}_3\text{AH}_6 \text{ (hydroganet)} \tag{2.8}
\]

C₃A is the most reactive towards water and is believed to have a significant influence in the early hydration of Portland cement (Barnes, 1983). It should be noted that the presence of C₃A could be an undesirable feature because it lends itself to “sulphate attack”, which is a common cause of cement deterioration. Further discussion on sulphate attack can be found in Chapter 7 of the thesis.

The hydration of the ferrite phase is very similar to that of C₃A, both in the presence and absence of gypsum, although the hydration rate is much slower (Barnes, 1983). The resultant product is a solid solution of C₃(AF).6H. The effect of gypsum on the rate of reaction is greater than that on C₃A. As the iron content of this phase increases, the rate of hydration decreases. In the reaction products, iron oxide plays the same role as alumina, with Fe₂O₃ substituting for Al₂O₃ (Gani, 1997).

Chemically, the hydration process is a complex dissolution-precipitation process in which, unlike the previously described hydration of individual clinker minerals, the various hydration reactions proceed simultaneously at differing rates and influence each other. Table 2.6 provides an overview of the hydration process of OPC. In general, it is believed that there are three basic stages of hydration involved:
1) **Early Period (0-3h):** Possibly a diffusion-controlled slow reaction that ends at the time of initial set (Jennings, 2000). The C₃S becomes coated with a gelatinous layer, which has the morphology of exfoliating films. Small rods of AFt are also observed to form outside this layer. CSH layers start to form fibrils at the end of this period (Gani, 1997).

2) **Middle Period (~3-24h):** There is rapid growth of both CSH and calcium hydroxide that results in the setting of the cement paste (Gani, 1997). Small grains of cement are covered with fibrils to form rosettes or spherulites, and long rods of AFt develop after about 16hr. This nucleation and growth stage last up to 24h (Jennings, 2000).

3) **Late Period (>24h):** This is another diffusion-controlled stage, for the remaining duration of the reaction (Jennings, 2000).

The dissolution of anhydrous phases enables the formation of compounds whose solubilities are lower than those of the anhydrous clinker minerals, thus leading to the precipitation of colloidal and crystalline hydrates that form the hardened paste (Barnes, 1983). Although most of the mineral constituent of OPC reacts with water within the first few days, the rates at which the individual compounds react are different, their reactivities are roughly in the order: C₃A>C₃S>C₄AF>C₂S, however the actual rate of hydration will be further affected by the presence of impurities, particle size, crystal size, concentration of crystal imperfections, crystallinity, polymorphic form of some of the clinker components and the actual curing condition (Gani, 1997; Barnes, 1983; Taylor, 1964). Table 2.7 shows the typical composition and properties of hardened cement paste made from OPC.

Since each of the four constituents behaves differently in the system, by adjusting the relative amount of the phases present, the properties of cement can be altered accordingly. Different types of cement will hence be produced to suit different requirements. For example, rapid setting cement contains high C₃S content, while low heat cement contains less C₃S and C₃A. Moreover, many other special cements have been developed for a wide range of applications e.g. high alumina cement, polymer-modified cement, and supersulphated cement, which is resistant to sulphate.
attack. Refer to the work of Gani (1997) for a general review on the properties, the production, characterisation and the reaction mechanism in these special cements.

2.2.4 Calcium Silicate Hydrate (CSH)

Calcium silicate hydrate (CSH) gel is believed to be the predominant constituent in the hydrated Portland cement (Barnes, 1983). More importantly, it constitutes the major binding phase in Portland cement, and it is believed to be responsible for the strength development in OPC (Gani, 1997; Taylor, 1964).

Despite the discovery of OPC since the 1800s, the structure (in both atomic and nanometer scale structure) and the morphology of CSH gel formed are still under active investigation (Hong and Glasser, 2002; Olson and Jennings, 2001; Schneider et al., 2001; Tennis and Jennings, 2000; Escalante-Garcia et al., 1999; Faucon et al., 1999, 1998a, 1998b and 1997; Rahman et al., 1999; Richardson, 1999; Yu et al., 1999a; Richardson and Groves, 1997, 1993; Cong and Kirkpatrick, 1996; Garboszi and Bentz, 1996; Moss et al., 1996; Chatterji, 1995).

Groves, Richardson and Brough in particular have published extensively on the nature of the CSH gel formed in various cementitious systems using electron microscopy and nuclear magnetic resonance (NMR) (Brough and Atkinson, 2002; Brough et al., 2001, 2000, 1996, 1995; Richardson, 1999; Richardson and Groves, 1997, 1993, 1992; Richardson et al., 1994; Rodger and Groves, 1989; Groves et al., 1986).

Jennings and his co-workers have also published extensively, especially in the area of the modelling of the microstructure of CSH gel using various other techniques such as neutron scattering (Juenger and Jennings, 2002, 2001; Rothstein et al., 2002; Olson and Jennings, 2001; Jennings, 2000; Song et al., 2000; Tennis and Jennings, 2000; Berliner et al., 1998; Thomas et al., 1998; Moss et al., 1996). With the advancement in analytical techniques and the incorporation of computerised operation units, the examination of the various aspects of CSH gel has become more sophisticated, and yet there are still a lot of questions to be answered.

It is known that a considerable amount of impurity oxide (e.g. alumina, iron, alkali) can be adsorbed into the CSH structure (Barnes, 1983). The elemental composition of
the CSH gel is dependent on the extent of the substitution and more importantly the nature of raw materials used. It is generally believed that the composition of CSH formed in the hardened OPC is very similar to that present in the hardened C₃S, but contains a smaller amount of aluminium substituted for silicon (Richardson and Cabrera, 2000). Moreover, the composition and the morphology of the CSH gel change with time and environmental condition (e.g. relative humidity, temperature), and a number of CSH gels have been identified and studied (Gani, 1997; Barnes, 1983; Taylor, 1964). With the incorporation of different admixtures (e.g. pozzolan, plasticisers) and additives used in modern cement production, the structure of CSH gel, especially in the nanometer scale, has become even more complex and controlled by zones with special microstructures, that occur in specific places in the system, instead of the prevalent general microstructure (e.g. aggregate-cement paste interfacial zone) (Gleize et al., 2003). All these factors discussed here are some of the reasons, which make the study into the microstructure of OPC based materials complex.

2.2.4.1 Morphology of CSH

The CSH gel formed is essentially amorphous to semi-crystalline. Gani (1997) described the morphology of CSH gels as fibrous or in the form of about 1nm thick layers, which may be rolled up, distorted or stacked up. The gels coat the cement grain surface, and they may be completely amorphous, or consist of very fine crystallites. Other researchers suggest that CSH could exhibit three or four morphologies (Gleize et al., 2003):

- Type (1) Acicular - elongated fibrous-acicular form with spines or needles;
- Type (2) Honeycomb - reticulated networks,
- Type (3) Compact - denser-almost sphere form and is formed when less space is available for particle growth, and
- Type (4) Compact - similar to Type (3) with a more dimpled morphology.

It is believed that the differences between Type (3) and Type (4) are not significant, in which Type (4) has a more dimpled morphology and is likely to result from a transformation in situ of anhydrous phase when the system has even less space remaining and low ionic mobilities (Barnes, 1983).
Thomas and co-workers (Thomas et al., 1998) suggested that based on the evaluation of the surface area of a cement paste as measured by neutron scattering, there exist two different types of CSH morphology: one with a high-surface area form, which rapidly fills the available pore space during the early hydration, and the other, a low surface area form, which predominates at later times.

Richardson and co-workers (Richardson and Cabrera, 2000; Richardson and Groves, 1997) further classified these two distinct types of CSH morphology in any given system as: inner product (Ip) formed within the boundaries of the original anhydrous grains, and outer product (Op), formed in the originally water or solution-filled spaces. The Ip CSH region most commonly has a compact, fine-scale and homogeneous morphology, whereas the Op CSH exhibits a strongly linear, directional morphology. The Ip generally has a dense homogeneous morphology with only very fine porosity. The morphology of the Op CSH varies with chemical composition; it has a fibrillar morphology at high Ca/Si molar ratio, which gradually changes to foil-like with a reduction in Ca/Si ratio.

2.2.4.2 Structure of CSH

It is widely suggested that the CSH at the atomic scale can be visualised as tobermorite with many imperfections and it becomes nearly amorphous, possibly intermixed at a very fine scale with a similar version of jennite (Jennings, 2000; Richardson et al., 1994; Taylor, 1964). However, it is still unclear whether the CSH structure is homogeneous or heterogeneous at a scale greater than 1 to 10nm.

Given the high level of structural variations of the CSH gel, structural models of CSH are often developed to give researchers a better insight into the nature of CSH gel synthesised under different conditions (Tennis and Jennings, 2000). Figure 2.2 shows a diagram of a basic structure proposed for CSH (Faucon et al., 1998a, b). In Jennings' model (Jennings, 2000), the basic building block of OPC is modelled as a unit of CSH that is roughly spherical and approximately 2nm across with a specific surface area of about 1,000m²/g. These building blocks are postulated to flocculate to form larger units.
Taylor (Richardson et al., 1994; Taylor, 1986) proposed a model for the structure of CSH based on finite silicate units derived from the dreierkette structures of 1.4nm tobermorite and jennite by the omission of some or all of the bridging tetrahedral silicate. The omission of all bridging tetrahedral silicate thereby gives completely dimeric CSH. This dreierkette model has been widely adapted in the discussion and the interpretation on the microanalysis and NMR analysis conducted by Richardson and his co-workers (Richardson and Groves, 1997; Richardson et al., 1994).

Most models differ primarily in their interpretation of the effects of water on the pore structure and surfaces of the colloidal particles in the paste. It has been a common practice to examine specimens that have already been dried. Almost nothing is known about the interactions between the CSH and ionic species present in the pore solution (Barnes, 1983). Detailed discussion on the different CSH models will not be presented in the thesis. Readers are therefore advised to consult the works of different researchers, as discussed earlier, for a detailed discussion on the different CSH models.

2.2.4.3 Silicate Structure within the CSH

It is generally believed that hydration involves polymerisation of the monomeric silicate units originally present in the anhydrous calcium silicates, first to dimeric and then to polymeric silicate (Barnes, 1983). The CSH in young pastes consists mainly of dimeric silicate chains (Richardson, 1999); as hydration proceeds, some of the dimers are linked by monomers to form pentamers, and then possibly dimers and pentamers are linked by monomers to form octamers, thus giving a 2, 5, 8, ..., (3n-1) chain length sequence, where n = 1, 2, 3, etc (Richardson, 2000; Richardson and Groves, 1997). The polymeric silicates formed are linear chains with the predominant species having five or eight silica tetrahedra linked together. Only a small amount (if any) of monomeric silica is formed in CSH. Subsequently, the reduction in the amount of monomer present in CSH can be used to determine the degree of hydration (Barnes, 1983). In most systems, dimer is the predominant silicate species in CSH, with linear pentamer as the next most abundant, with some linear octamer (Richardson, 1999).
2.2.4.4 CaO/SiO$_2$ Molar Ratio

A major variable in the CSH gel also includes the molar ratio between CaO and SiO$_2$ (C/S ratio), which ranges from 0.6 to 2.5 (Phair, 2001). This ratio is of significance because it determines the interlayer structure within the CSH gel, in which it can greatly affect the properties of the gel (Rahman et al., 1999). Barnes (1983) and Gani (1997) found that the average bulk C/S ratio of the CSH gel lies in the range of 1.5-1.7, while Richardson (1999) found that the C/S ratio of CSH in neat Portland cement pastes varies from 1.2 to 2.3 with a mean value of ~1.75.

The estimation of the molar ratio between the CaO and SiO$_2$ of the CSH gel using a variety of analytical techniques has been an area of interest to cement researchers (Hong and Glasser, 2002; Olson and Jennings, 2001; Schneider et al., 2001; Escalante-Garcia et al., 1999; Faucon et al., 1999, 1997; Rahman et al., 1999; Richardson, 1999; Richardson and Groves, 1997, 1993; Chatterji, 1995), and it is often found to be a very useful parameter in analysing the CSH gel at different age and formed under different conditions.

For example, it was found that the C/S ratio of the CSH in young OPC pastes displays a bimodal distribution, which becomes unimodal as the paste matures (Richardson, 2000; Richardson and Groves, 1993). Richardson (2000) has further suggested that the average C/S ratio remains essentially constant with degree of hydration, despite the nanostructure of CSH formed in hardened C$_3$S and C$_2$S pastes changing as the hydration proceeds.

Due to the highly heterogeneous nature of the microstructure and morphology of the resultant geopolymer product synthesised in the work reported in the thesis, it is not possible to easily distinguish and identify the difference between various CSH gels formed using electron microscopy and other techniques. Subsequently, the estimation of the C/S ratio of the CSH gel formed in various systems is a main parameter used throughout the thesis in identifying various CSH phases present in the resultant product. As demonstrated in this section, the C/S ratio is indeed a valid, efficient and effective way in studying the different CSH structure.
2.3 Alkaline Activated Cementitious Materials

2.3.1 Overview

As discussed in the previous section, the properties of cement can be altered simply by adjusting the relative amounts of the four main phases (C₃S, C₂S, C₃A and C₄AF) present in Portland cement. Moreover, admixtures can be added to the cementitious system to alter the properties of resultant binders. An admixture is formally defined by the American Concrete Institute (ACI) as ‘a material other than water, aggregates, hydraulic cement and fibre reinforcement, used as an ingredient of concrete or mortar, and added to the batch immediately before or during its mixing’ (ACI Committee 212, 1989).

There are hundreds of admixtures currently available and they can be grouped based on their different effects, including: air-entraining agents, accelerating/retarding agents, water reducer/plasticisers, bonding admixtures, water-repelling agents, pigments, pore fillers and mineral admixtures. This section will focus on the effect of mineral admixtures (e.g. pozzolans including metakaolin, flyash and granulated blast furnace slag) on the cementitious system, in which this will lead to the further discussion on another class of cement – alkaline activated cement, which is postulated to form a link between the chemistries of OPC and geopolymers (Section 2.3.3). Readers are advised to consult the works of Jackson and Dhir (1996) and Gani (1997) for a more detailed overview on how other admixtures affect the OPC system.

2.3.2 Pozzolan - Portland Blended Cement

Pozzolans are formally defined as a siliceous or siliceous and aluminous materials which in themselves possess little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties (ASTM C618-93). In other words, pozzolanic materials do not set if mixed with pure water alone. When alkali solution is added to the system, pozzolanic materials will set and behave like a cementitious material. Pozzolans are often added to Portland cement in order to (1) improve properties of the resultant binder, (2) reduce heat evolution during setting, (3) reduce cost, and (4) improve durability (Gani, 1997).
A considerable amount of research has been conducted on both the physical and chemical effects of different pozzolans (e.g. metakaolin, silica fume) on the OPC system. Individual chemical mechanisms involving different pozzolans have been proposed and investigated with the aim of improving the durability and other physical properties of the concrete (Rodriguez-Camacho and Uribe-Arif, 2002; Duchesne and Berube, 2001; Ferraris et al., 2001; Frias and Cabrera, 2001; Hanehara et al., 2001; Paya et al., 2001; Anderson et al., 2000; Frias et al., 2000; Gallias et al., 2000; Poon et al., 2000; Ramlochan et al., 2000; Zelic et al., 2000; Li et al., 1999; Papadakis, 1999; Malhotra and Mehta, 1996; Uchikawa et al., 1996; Wild et al., 1996; Zhang et al., 1996; Toutanji and El-Korchi, 1995; Zhang and Malhotra, 1995; Frigione and Sersale, 1989). However, in general, there is still a lack of published literature detailing the effect of the mineral admixtures on the chemical mechanisms involved as well as the chemical bonding created or destroyed during the process. A thorough understanding of the chemical and mechanistic effects on the resultant binder is essential to improve the physical properties of the concrete.

The pozzolans commonly used in cement production can be classified into two main groups: natural pozzolans (e.g. volcanic ash) and artificial pozzolans (e.g. flyash and granulated blast furnace slag - GBFS). Most of the pozzolanic materials used today are industrial by-products, which require relatively little energy for use. More importantly, the utilisation of industrial by-products as a pozzolanic admixture will reduce the disposal cost incurred and reduce the volume of cement production, which will further reduce the environmental impact of the cement industry as discussed earlier in Section 2.1. For example, the energy required to grind granulate blast furnace slag is only approximately 10% of the total energy required for the production of Portland cement (Shi and Qian, 2000). Readers are advised to refer to the work of Malhotra and Mehta (1996) for a more comprehensive review of the composition and performance of important pozzolanic and cementitious admixtures.

It has been suggested that the incorporation of pozzolan will have three primary actions in a cementitious system in enhancing the strength and durability of concrete: (1) filler effect, (2) the acceleration of OPC hydration, and (3) the rapid removal of calcium hydroxide from the system through the pozzolanic reaction (Equation 2.9) (Poon et al., 2003; Wild et al., 1996). It has been recognised for a long time that the
use of mineral admixtures generally improves the durability of concrete. Many authors have concluded that pozzolanic cements or blends with slag, flyash, or silica fume are best suited for applications where durability is a priority requirement (Roy et al., 2000).

When water is added to a mixture of cement, sand and a pozzolan, the calcium hydroxide produced mainly from the hydration of C₃S and C₂S in OPC (as shown by Equations 2.2 and 2.3) will react with the silica (and alumina) from pozzolan. The reaction between the pozzolan and calcium hydroxide will produce the CSH gel and this is generally known as the pozzolanic reaction (Gani, 1997). Equation 2.9 below describes a general representation of the pozzolanic reaction:

\[
\text{Ca(OH)}_2 + \text{SiO}_2 \text{(pozzolan)} \rightarrow \text{CSH} \tag{2.9}
\]

It is commonly agreed that the presence of a reactive phase, such as calcium hydroxide, in the hydrated product could lead to the deterioration of the cement mortar. The incorporation of a pozzolan will reduce the amount of calcium hydroxide present and at the same time convert the Ca(OH)₂ to CSH, which will provide better binding property and therefore improve the mechanical strength of the binder. The rate of strength development is generally affected by the addition of pozzolan due to the slower rate of hydration in comparison to Portland cement (Gani, 1997).

The important consequences of the pozzolanic reaction is the reduction and even the elimination of free Ca(OH)₂ in the silica-rich system. The reaction is similar to an acid-base reaction: the alkaline Ca(OH)₂ reacts with the more “acidic” silicate components (Glasser, 1997). The subsequent reduction in pH is important, because the principal reaction product, CSH, is itself sufficiently soluble under conditions of a relatively high pore fluid pH, ranging from ~12.5 for high calcium CSH to approximately 10.5 for low lime CSH (C/S = 1.0) (Glasser, 1997).

The extent to which the pozzolanic reaction takes place in a cementitious system can be determined by quantifying the amount of calcium hydroxide consumed as the paste matures and new pozzolanic reaction products form (van Jaarsveld, 2000). Isaia et al. (2003) suggested that the pozzolanic effect depends not only on the pozzolanic
reaction but also on the physical or filler effect of the smaller particles in the mixtures. When the small particles of pozzolan are dispersed in the OPC, they generate a large number of nucleation sites for the precipitation of hydration products. Subsequently, this mechanism makes the paste more homogeneous and dense as for the distribution of the finer pores (Isaia et al., 2003)

It is generally believed that a combination of glassy or poorly crystalline structures and high surface areas is the cause for the reactivity of the aluminosilicate phase present in pozzolans with calcium hydroxide (Malhotra and Mehta, 1996). The pozzolanic and cementitious properties of different mineral admixtures, which govern the strength development and permeability of the blended cement system, are profoundly controlled by mineralogical characteristics as well as the granulometric characteristics (including particle size and surface area of the admixture) (Malhotra and Mehta, 1996). The water demand and workability of OPC are controlled by particle size distribution, packing effect, and smoothness of surface texture of the admixtures. On the whole, the elemental composition of pozzolans does not have any significant effect on the pozzolanic reactivity. In most cases, the mineralogical composition of the pozzolan is further dependent on the conditions of the processing of formation, which cannot be changed during the manufacturing of cement. The control of particle size distribution is the only parameter that can be used in altering the pozzolanic or cementitious activity of any given source material.

As discussed in Section 2.2.3, the major phases present in hydrated OPC are: CSH, calcium hydroxide and a combination of AFt and AFm. The introduction of pozzolan into the system will alter the quantity of these phases, the composition of AFm and the composition and morphology of the CSH gel (Richardson and Groves, 1992). The analysis of the CSH gel produced by the pozzolanic reaction is difficult due to the unknown amount of calcium consumed in the reaction and it was suggested that the C/S ratio of the CSH formed may be lower than that in neat CSH formed in OPC system (Olson and Jennings, 2001; Richardson and Groves, 1992).

With a rich variety of pozzolan being used currently in the cement industry, it is not possible to generalise on the nature and composition of the resultant products formed in a pozzolan-Portland blended cement system. For example, amorphous silica from
rice husk was found to react with the Ca(OH)$_2$ in forming a kind of CSH gel (Ca$_{1.8}$SiO$_{3.5}$·xH$_2$O), that filled in pores and played a bridging role between hydrates and unhydrated cement particles (Yu et al., 1999b). On the other hand, strätlingite (C$_2$ASH$_8$) and CSH gel were found to be the dominant phases formed in the metakaolin blended cement with detectable amount of C$_4$AH$_{13}$ (Frias and Cabrera, 2001). These two examples have highlighted that the difference between the nature of the resultant product synthesised from different systems is quite significant, and therefore it is not possible to discuss each individual chemistry involved here. Instead, a substantial extent of discussion with associated references on the metakaolin/cement and slag/cement blended systems will be given throughout the thesis when these systems become more relevant to the current investigation.

2.3.3 Alkaline Activated Cement (AAC)

It was shown in the previous section that pozzolans are added to OPC system to enhance the properties of the resultant product. With the favourable and promising properties shown by the incorporation of pozzolans to an OPC system, the focus of research has moved towards a new class of cement with the binding property almost entirely based on reactions (e.g. the pozzolanic reaction) other than the traditional hydration process of OPC. In contrast to the pozzolan-Portland blended cement, there is a much larger replacement or even a total replacement of cement with pozzolans (especially granulated blast furnace slag (GBFS), flyash and metakaolin) in an alkaline activated cementitious system.

With an increasing amount of pozzolans being used in the system, the amount of calcium hydroxide present (produced as one of the products in the hydration of OPC) is not sufficient to provide the necessary alkali to activate the pozzolans. Thus, an external alkaline activator has to be added to the system. This new class of cement is generally known as alkaline activated cement (AAC), and refers to any system that uses an alkali activator to initiate a reaction or a series of reactions that will produce a material that possesses cementitious properties. It includes alkali activated slag and/or flyash, and geopolymers (a three-dimensional amorphous alkali aluminosilicate network).
The inclusion of geopolymers in this section, as an example of alkaline activated cement is likely to cause some controversy and confusion. This is mainly due to the diverse terminology used in the field and the fact that geopolymers are formed through a chemical mechanistic path with a reaction product entirely different to the CSH gel. However, due to the high degree of overlapping in raw materials used and applications, geopolymers are included as a special class of AAC, which can also be separated into a new class of materials. In fact, it is one of the aims of the thesis to demonstrate the link between OPC, AAC, and geopolymers; whereby the chemistry of the AAC system is somewhere between OPC and geopolymer. The discussion on the formation of both CSH and geopolymeric gels simultaneously within a single system lays the foundation of the thesis. A comprehensive review on geopolymers will be presented in Section 2.4. This section will focus on the alkaline activated system based on the formation of CSH gel.

Alkali-activated cement has been developed in the former USSR and in other countries for more than thirty years, and is characterised by high strength, lower heat evolution, high resistance to chemical attack and low porosity (Wu et al., 1990). It is generally believed that various forms of CSH gel are responsible for the binding property in most AAC systems (Taylor, 1964), however the exact nature of the reaction products has been a constant debate topic amongst researchers. This is most likely attributed to the great degree of variation in the CSH gel formed in an alkaline activated system.

The nature of the resultant product in an alkaline activated system is believed to be dependent on a number of factors including: mineralogical composition and particle size distribution of raw material, strength and nature of alkaline activator, and curing conditions. It is generally agreed that the nature of CSH gel formed in AAC is expected to be different and more amorphous (poorly crystalline) than the one formed in OPC (e.g. different C/S ratio, morphology and crystallinity) (Puertas and Fernandez-Jimenez, 2003; Wang and Scrivener, 1995; Krivenko, 1994; Shi and Day, 1995; Wu et al., 1990), however, in most cases, researchers fail to quantify this fully.

A substantial amount of research has been conducted on various aspects of alkaline activated cement (Hong and Glasser, 2002; Krivenko et al., 1999; Brough et al., 1996;
Krivenko, 1994; Pundi, 1994; Way and Shayan, 1989). The history, development, and opportunities and challenges faced by alkaline activated cement have been extensively reviewed (Roy, 1999). Alkaline activated slag (Brough and Atkinson, 2002; Krizan and Zivanovic, 2002; Kim and Hong, 2001; Bakharev et al. 2000; Brough et al., 2000; Collins and Sanjayan, 2000; Li and Yao, 2000; Song et al., 2000; Shi and Day, 1995; Wang and Scrivener, 1995; Richardson et al., 1994; Douglas et al., 1991; Douglas and Brandstetr, 1990; Wu et al., 1990), flyash (Brough et al., 2001; Li et al., 2000a; Palomo et al., 1999a; Shehata et al., 1999; Bleszynski and Thomas, 1998) and slag/flyash blended systems (Puertas and Fernandez-Jimenez, 2003; Agyei et al., 2000; Fu et al., 2000; Li et al., 2000b; Puertas et al., 2000), in particular, have been widely studied in the past thirty years.

Richardson, Brough and Groves have done extensive research on the chemical mechanism and microanalysis of the structure of OPC and AAC during the setting and hardening state (Richardson and Cabrera, 2000; Groves and Richardson, 1994; Richardson et al., 1994; Richardson and Groves, 1992). Krivenko has presented an extensive account on the chemical mechanism of the formation of alkaline activated cement (Krivenko, 1994). Despite extensive research on OPC and AAC, the mechanistic relationship between OPC and AAC is still not well studied.

In general, the alkaline activated flyash often behaves more similarly to geopolymers with its binding property based on the formation of an alkali aluminosilicate network, rather than a CSH gel. Further discussion on the alkaline activation of flyash will also be presented in Section 2.4. A detailed review on the alkaline activation of GBFS in the present work, in which CSH gel is the main contributor to the binding property, will aid readers in understanding the further work presented in the thesis; especially in Chapter 4, in which GBFS is the principal calcium source investigated.
2.3.4 Alkaline Activated Granulated Blast Furnace Slag

The principle of alkaline activation of granulated blast furnace slag (GBFS) has been known since the 1940s (Shi and Qian, 2000). It is believed that the hydraulicity of the slag is affected by various factors, including the composition, the glass content, and the particle size distribution (Richardson and Groves, 1992). Granulated blast furnace slag is a by-product of the iron industry and consists mainly of calcium-(magnesium) aluminosilicate glass. Slag has a variable composition depending on the raw materials and the industrial process used, thus, it is not possible to generalise on the reactivity of slag. In general, there is still a lack of understanding of the reactivity, reaction and chemical mechanism in the alkaline activated GBFS system.

The use of alkaline solution to activate the GBFS will enhance the specific surface area of the hydration product of GBFS to a much greater extent than for the normal Portland cement hydration product (Roy et al., 2000). A range of alkaline activators has been used in activating the GBFS, including calcium hydroxide, sodium carbonate and silicate. Shi and Day have demonstrated that the nature and dosage of the alkaline activator, the curing temperature and the water to slag ratio all have a significant effect on the hydration and structure development of the alkali-activated slag (Shi, 1996; Shi and Day, 1996). This includes the effect on the strength development, pore structure development and water/chloride permeability (Shi, 1996). However, regardless of the type of activator used, the main hydration product is CSH with low C/S ratio and varying degrees of crystallinity (Wang and Scrivener, 1995).

It is generally accepted that the product from the alkaline activation of GBFS consists mainly of CSH of a low C/S ratio with AFm, and hydroalcite (crystalline phase), while normal Portland cement consists mainly of CSH with a high C/S ratio, Ca(OH)$_2$ and ettringite (AFT) (Roy et al., 2000; Shi and Qian, 2000; Wang and Scrivener, 1995; Richardson et al., 1994). Using NMR and TEM techniques on the hydrated product of the alkaline activated slag system, Richardson et al. (1994) suggested that the CSH gels formed are related by both composition and morphology to the CSH gels present in slag-OPC blended paste, but are more crystalline. In an alkaline activated cement-slag blend, with increasing amount of GBFS present, the fibrillar (linear, directional) morphology is gradually replaced by the foil-like morphology as well (Richardson, 1999). Richardson (1999) further suggested that the hydration products and
microstructure obtained by alkaline activation are similar to water activation with the difference that the calcium hydroxide formed is microcrystalline and the CSH is structurally better ordered.

Glasser (1996) suggested that the rate of reaction of the glassy phase in GBFS is accelerated in alkaline solutions because the initial stage of the reaction requires hydrolysis. The glass contains bonds of the type Si-O-Si and these are hydrolysed by OH'. Once the glass network is disrupted, reaction between components, including solid activator, occurs. In the early stages of reaction with solid activators, much material transport occurs through solution. However, as precipitation increasingly builds up a solid matrix, and as liquid water becomes increasingly confined to pores, transport through the solid, often gel-like products of reaction dominates continuing reaction.

The kinetics of slag hydration are generally believed to be difficult to measure directly due to the heterogeneous nature of the raw GBFS, as well as the resultant product. Fernandez-Jimenez and co-workers (1999) suggested that the reaction mechanism for alkaline activated slag was a diffusion mechanism with an activation energy of 57.6kJ/mol. While Wang and Scrivener (1995) suggested that the products were formed by a dissolution and precipitation mechanism during the early stages of reaction, but at later stages, the reaction may continue with a solid state mechanism in an alkaline activated slag system. Further hydration of the alkaline activated slag system will also be dominated by the reaction of the anion or anion group of the activator and the Ca$^{2+}$ dissolved from slag to form calcium compounds less soluble than Ca(OH)$_2$, rather than the initial pH of the activator solution (Shi and Day, 1995, 1996).

With the much higher aluminium content in slag than in OPC, it is more likely to have aluminium, substituting silicon in the CSH structure. It was reported that the aluminium present in CSH in the alkaline activated slag system is in the predominantly 4-fold coordination and that aluminium occupies the bridging tetrahedral sites of the dreierketten silicate chain structure (Richardson et al., 1994). There is substantial amount of evidence that slag glasses with Al in 4-coordination are more reactive than those glasses having Al in 6-coordination (Shi, 1996). However, it
is still unclear whether this is universal or compositionally dependent. When there is increasing amount of aluminium substituting the silicon in the silicate chain, this gradually leads to a new material with the dominant binding property coming from the aluminosilicate network. This also links the discussion to the next category of alkaline activated system, geopolymers, whereby the binding property is based on the formation of a three-dimensional alkaline aluminosilicate network.

2.4 Geopolymers

2.4.1 Overview

Cementitious materials based on Portland cement are the most common materials used in the construction industry. However, with the increase in energy cost and the environmental and social problems associated with the CO$_2$ (greenhouse) emission in the manufacturing of Portland cement as discussed earlier, an alternative construction material is needed. Geopolymers offer an environmentally friendly and cost effective material that could be used in substitution for Portland cement.

Geopolymers are new age materials with a wide range of applications in the construction industry and also for toxic waste treatment. The development of geopolymers and geopolymerisation can be traced back to the 1970s when Davidovits, a French scientist, first proposed that geopolymers are formed by the polymerisation of individual aluminate and silicate species, which are dissolved from their original sources at high pH in the presence of soluble alkaline metals (Davidovits, 1991; Davidovits and Davidovics, 1988).

The nature of the resultant geopolymeric binder is dependent on the elemental and mineralogical compositions of the aluminosilicate source, the quantity and the nature of the alkaline activator used in activation, and the curing conditions (e.g. humidity and temperature). Metakaolin and flyash have been the most studied aluminosilicate source materials in geopolymerisation (Hadjito __et al__, 2002; Lee and van Deventer, 2002a, b, c, d; Phair and van Deventer, 2002b, 2001; Subaer __et al__, 2002; Swaanepoel and Strydom, 2002; van Jaarsveld __et al__, 2002; Xu and van Deventer, 2002b; Phair, 2001; Phair __et al__, 2000; van Jaarsveld, 2000; Krivenko __et al__, 1999; Silva __et al__, 1999;
van Jaarsveld and van Deventer, 1999a, b; Katz, 1998; Catalfamo et al., 1997; Silverstrim et al., 1997; Palomo and Glasser, 1992). Xu and co-workers investigated a range of natural aluminosilicate minerals as the possible aluminosilicate source in geopolymerisation, and these natural minerals were shown to have promising ability (Xu, 2002; Xu and van Deventer, 2002a, b, 2000; Xu et al., 2001).

Although the exact chemical structure of geopolymers has not been determined, in general, geopolymers are often viewed as the amorphous version of zeolites with a three-dimensional aluminosilicate forming the backbone of the structure (Davidovits, 1999a). Geopolymeric binders have similar chemical composition as natural zeolitic materials, but without having an extensive crystalline zeolitic structure (van Jaarsveld, 2000). Unlike conventional Portland cement, geopolymers do not rely on the presence of CaO, and are not dissolved by acidic solutions (Davidovits, 1999a).

Geopolymers can be rapidly moulded into different shapes at low temperature (a few hours at 30°C or a few minutes at 80°C or a few seconds with microwave). They can behave as thermosetting organic resins but are stable up to 1000-1200°C, whereas organic resins are not (Davidovits, 1991; Davidovits and Davidovics, 1988). Geopolymers exhibit unique high performance properties including: rapid strength gain (up to 90% of ultimate in 24h), high ultimate strengths (over 110MPa), low shrinkage, excellent acid resistance, superior refractory properties, corrosion resistance, hard but smooth surface, thermal stability, precise moldability, and freeze-thaw resistance (Davidovits et al., 1998, Silverstrim et al., 1997). The major applications of geopolymeric materials and geopolymer technology are mostly in the construction industry (as a possible alternative to OPC), fire resistant composites, immobilisation of heavy/toxic metals, and transformation of waste materials (e.g. flyash) into useful construction materials.

The majority of the fundamental research on geopolymerisation undertaken in recent years can be summarised into the following five main categories:

(1) Characterisation of geopolymers using different source materials (Hardjito et al., 2002; Phair and van Deventer, 2002a, b, 2001; Subaer et al., 2002; Swanepoel and Strydom, 2002; Xu, 2002; Xu and van Deventer, 2002a, b,
2000; Phair, 2001; Barbosa et al., 2000, 1999; Granizo et al., 2000; van Jaarsveld, 2000; Davidovits, 1999a, b, 1994, 1991, 1984, 1982; Palomo et al., 1999a, b; Davidovits et al., 1998, 1990; Katz, 1998; Rahier et al., 1997, 1996a, b; Silverstrim et al., 1997; Palomo and Glasser, 1992; Palomo et al., 1992a, b; Davidovits and Davidovics, 1988);

(2) Improvement of the physical and chemical properties of the geopolymers (Lee and van Deventer, 2002c, d, 2001; Phair and van Deventer, 2002a; Phair et al., 2001, 2000; Lyon et al., 1997);

(3) Effect of Na\(^+\)/K\(^+\) in geopolymerisation (Phair, 2001; Xu et al., 2001; van Jaarsveld, 2000), and

(4) Effect of the different anionic additives (Lee and van Deventer, 2002a, b, c, d, 2001);

(5) Immobilisation of heavy metals using geopolymerisation (Phair, 2001; Phair and van Deventer, 2002a, 2001; van Jaarsveld, 2000).

This section will therefore focus on the development and the current advancement of geopolymer technology. In addition, it will also introduce the relationship between the chemistries of OPC and geopolymer, which will form the basis of the thesis.

### 2.4.2 Definition, Terminology and Basic Structure

Geopolymerisation involves the chemical reaction of alumino-silicates oxides (Al\(^{3+}\) in IV-fold co-ordination) with alkali polysilicates in the presence of hydroxide ions, yielding polymeric Si-O-Al bonds (van Jaarsveld, 2000; Davidovits et al., 1998). The silicon and aluminium tetrahedra are joined together in three directions by sharing oxygen atoms. It is thought that cations (Na\(^+\), K\(^+\), Li\(^+\), Ca\(^{2+}\), Ba\(^{2+}\), NH\(_4^+\), H\(_2\)O\(^+\)) are present in the framework cavities to balance the negative charge of Al\(^{3+}\) in IV-fold co-ordination (Davidovits, 1999a). However whether these ions simply play a charge-balancing role or are actively bonded into the matrix is still unclear.

Theoretically, any alkali and alkali earth cation can be used as the alkaline element in the reaction, however the majority of research has, so far, focused on the effect of sodium (Na\(^+\)) and potassium (K\(^+\)) ions (Xu, 2002; Phair, 2001; van Jaarsveld, 2000; Davidovits, 1999a). It has not been clearly proven whether other alkali and alkali earth cations, including calcium will participate in the reactions in a similar way.
The resultant geopolymer products synthesised at ambient temperature are believed to be amorphous to semi-crystalline three dimensional aluminosilicate structures, which are commonly referred to as polysialates (Davidovits, 1999a). Davidovits suggested that geopolymeric products are crystalline in structure only if they are synthesised at a hydrothermal setting and hardening temperature in the 150 to 180°C range (Davidovits, 1999a, 1994, 1991). The empirical formula for polysialates is as shown in Equation 2.10:

$$M_n(-SiO_2)_{z-2}AlO_2)_{n-z}wH_2O$$  \hfill (2.10)

Where M is the alkaline element, - indicates the presence of a bond, z is 1, 2, 3 or >3 and n is degree of polymerisation. Based on the Davidovits’ definition (Davidovits, 1999a), the type of polysialate formed is dependent on the Si:Al molar ratio:

- Poly(sialate) $M_n(-SiO-Al-O-)_{n}$  \hspace{1cm} M-PS \hspace{1cm} Si/Al=1:1
- Poly(sialate-siloxo) $M_n(-SiO-Al-O-Si-O)_{n}$  \hspace{1cm} M-PSS \hspace{1cm} Si/Al=2:1
- Poly(sialate-disiloxo) $M_n(-Si-O-Al-O-Si-O-Si-O-)_{n}$  \hspace{1cm} M-PSDS \hspace{1cm} Si/Al=3:1

For Si:Al >>3:1, the polymeric structure results from the cross linking of polysilicate chains, sheets or networks with a sialate link (-Si-O-Al-O-) (2D or 3D cross-link). Table 2.8 shows the classification and the major application of these different types of geopolymers.

Figure 2.3 shows a 3D-structure of a metakaolin-based geopolymeric binder as proposed by Davidovits (Davidovits, 1994a). It should be noted that this is purely a conceptual model, and that the true structure of a geopolymer has still not been determined. Geopolymeric binders have similar chemical composition as natural zeolitic materials, but without the distinctive zeolitic structure.

The amorphous nature of geopolymers synthesised at ambient temperature is believed to be due to the substantially faster setting time than zeolites, resulting in an amorphous to semicrystalline product with some zeolitic properties. Xu (2002) suggested that geopolymerisation comprises leaching, diffusion, condensation and
hardening steps, in contrast to the process of zeolite synthesis, which consists of prenucleation, nucleation and crystal growth. Moreover, the concentration of precursor species before solidification occurs is much higher in the case of geopolymerisation than in the case of the zeolite formation (van Jaarsveld, 2000). Table 2.9 summarises the major differences between the synthesis of zeolites and geopolymers.

### 2.4.3 Chemistry of Geopolymerisation

Despite extensive research, there is still no accepted universal chemical mechanism for geopolymerisation. The difficulties in analysing the heterogeneous nature of most of the aluminosilicate sources (e.g. flyash) and the amorphous nature of the resultant product formed, make the elucidation of a chemical mechanism difficult.

It has been shown so far that the resultant product is highly dependent on the nature of aluminosilicate source used, the nature and strength of alkaline activator and the curing condition. Subsequently, it is proposed that the reaction path taken in each system will also be different to some extent with various other side reactions taking place simultaneously. However, the fundamental geopolymerisation process is expected to be based on the equations Davidovits schematised as shown by Equations 2.11 to 2.14, with the synthesis being carried out through oligomers (dimer, trimer), which provide the actual unit structure of the three dimensional macromolecular edifice (Davidovits, 1999a, 1994, 1991):

\[
\text{NaOH/KOH} \quad (\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2)_n + 3n\text{H}_2\text{O} \rightarrow n(\text{OH})_3 - \text{Si}-\text{O}-\text{Al}^\text{1}\text{'}-(\text{OH})_3 \quad (\text{Orthosialate})
\]

\[
\text{NaOH/KOH} \quad n(\text{OH})_3 - \text{Si}-\text{O}-\text{Al}^\text{1}\text{'}-(\text{OH})_3 \rightarrow (\text{Na, K})-(\text{Si}-\text{O}-\text{Al}^\text{1}\text{'}-\text{O}-)n + 3n\text{H}_2\text{O} \quad (\text{Na,K}-\text{poly(sialate})
\]
NaOH/KOH
\[(\text{Si}_2\text{O}_5, \text{Al}_2\text{O}_2)_n + n\text{SiO}_2 + 4n\text{H}_2\text{O} \rightarrow n(\text{OH})_3 - \text{Si-O-Al}^+\text{O-Si-(OH)}_3 (2.13)\]
\[\text{(OH)}_2\]
(Ortho(asilicate-sioloxo))

NaOH/KOH
\[n(\text{OH})_3 - \text{Si-O-Al}^+\text{O-Si-(OH)}_3 \rightarrow (\text{Na},\text{K})-(\text{-Si-O-Al}^+\text{O-Si-O})_n + 4n\text{H}_2\text{O} (2.14)\]
\[\text{(OH)}_2\]
\[\text{O} \quad \text{O} \quad \text{O}\]
(\text{Na,K}-poly(asilicate-sioloxo))

Rahier and co-workers examined the properties of an amorphous glassy aluminosilicate, similar to geopolymers, which was referred to as the "low-temperature synthesised aluminosilicate glasses" or "low-temperature inorganic polymer glass" (Rahier et al., 1997, 1996a, b). This material was synthesised using metakaolin and sodium silicate solution. The following is the overall reaction as suggested by Rahier and co-workers:

**Aqueous solution (<100°C)**
\[(\text{Na}_2\text{O})(\text{SiO}_2)_{1.4}(\text{H}_2\text{O})_x + (\text{Al}_2\text{O}_3)(\text{SiO}_2)_2(\text{H}_2\text{O})_{0.05} \rightarrow (\text{Na}_2\text{O})(\text{Al}_2\text{O}_3)(\text{SiO}_2)_{3.4}(\text{H}_2\text{O})_z (2.15)\]

With \(z \sim 0.4\). The structure of this polymer is believed to consist of SiO\(_4\) and AlO\(_4\) tetrahedra randomly distributed, with the restriction that no Al-O-Al bonds occur (Rahier et al., 1996b). It was also suggested that the Si/Al molar ratio of the resultant product is dependent on the Na/Si molar ratio of the sodium silicate solution used (Rahier et al., 1996a).

Other researchers in particular Xu and van Deventer (Xu, 2002; Xu and van Deventer, 2000), have proposed a detailed chemical mechanism that takes place in each step of the geopolymerisation process. Generally, the mechanistic view of geopolymerisation can be summarised into the following five steps:
1. **Dissolution reaction.** Dissolution involves the formation of mobile precursors through the complex action of hydroxide ions. Aluminosilicates are dissolved in the alkaline solution to produce Si- and Al- monomers. The possible reaction as proposed by Xu and van Deventer (Xu, 2002; Xu and van Deventer, 2000) is shown in Equation 2.16, where $M^+$ is either Na$^+$ or K$^+$:

$$\text{solid Al-Si source} + \text{MOH} \Leftrightarrow M^{+}\text{OSi(OH)}_3 + M^{+}\text{Al(OH)}_4$$

(2.16)

monomer monomer

Xu and van Deventer suggested that this is a chemical hydration reaction, where the hydroxide ions hydrolyse the surface of the aluminosilicate (Al-Si) source and dissolve a small amount of Al and Si species to form their respective monomers (Xu, 2002; Xu and van Deventer, 2000).

This initial dissolution process is believed to be caused by the presence of hydroxide ions and is thought to be independent of the type or the concentration of the cations present (van Jaarsveld, 2000). However, the extent of leaching for both Al and Si is suggested to be dependent on the concentration of the alkaline solution, alkali metal cation in the solution, stirring speed, leaching period as well as the structure and composition of the aluminosilicate source material. The properties and characteristics of the aluminosilicate source, and the concentration of the alkaline solution, are believed to be the dominant factors (Xu, 2002).

2. **Diffusion.** Xu and van Deventer suggested that Al and Si species diffuse into the gel phase after being leached from the surface of the aluminosilicate particle (Xu, 2002; Xu and van Deventer, 2000). This therefore reduces the concentration of Al and Si species at the particle surface, thereby enhancing the further dissolution from the surface. A longer leaching period and a more intense stirring were found to improve the diffusion rate for the dissolved Al and Si species from the surface.

3. **Polymerisation.** Polymerisation of the lower ordered monomers will then take place to form the higher ordered dimer. The newly formed dimer may react
with another monomer or dimer or other Si- oligomers to form higher oligomers of varying geometries, i.e. linear, branched or cyclic. Equation 2.17 below is one of the possible formations of a dimer from monomers, with M being either Na or K.

\[ \text{OSi(OH)}_3 + \text{M}^+ \text{OSi(OH)}_3 + \text{M}^+ \Leftrightarrow \text{M}^+ \text{OSi(OH)}_2\text{-Si(OH)}_3 + \text{MOH} \]  

monomer monomer dimer

According to Xu and van Deventer, this reaction is the cation-anion pair condensation interactions based on Coulombic electrostatic attraction (Xu, 2002; Xu and van Deventer, 2000). There is no cation-anion pair reaction which exists for Al(OH)_4 tetrahedrons; consequently no Al-O-Al bonds are formed in the geopolymeric structure (Xu, 2002; Xu and van Deventer, 2000).

According to van Jaarsveld (2000), the main reason why Al-O-Al bonds do not form preferentially is due to a thermodynamic consideration. The Al-O-Al linkage has the highest free energy value amongst the three possible linkages during the polymerisation. The absence of Al-O-Al bonds in a geopolymeric structure is in agreement with Rahier’s finding as discussed earlier (Rahier et al., 1996b).

The other two possible linkages during polymerisation are Si-O-Si and Si-O-Al. However, the activation energy for forming an Al-O-Si linkage is lower than forming a Si-O-Si linkage. Subsequently, the polymerisation between Al complexes and Si complexes will take place in preference to the polymerisation between the Si complexes (Xu, 2002). The polymerisation between Al and Si will occur simultaneously along with the dissolution and diffusion steps as described earlier in Steps 1 and 2.

4. **Formation of Aluminosilicate Gel.** Formation of (-Al-O-Si-) bond network by reacting the M⁺ and the higher Si-oligomers.

5. **Polycondensation (Setting) and Hardening Process.** The exact mechanism by which geopolymer setting and hardening occurs is not fully understood. It was
believed that the geopolymeric gel is transformed to the final structure either through another dissolution and crystallisation or solid-state mechanism (van Jaarsveld, 2000).

Xu (2002) suggested that the hardening step in the geopolymerisation process is significantly different from the drying and hardening steps in zeolite synthesis. As reported by Xu (2002), this is because there is only evaporation of water and no chemical reaction involved during the drying and hardening step in zeolite synthesis. In contrast, there is no major movement of particles at this stage of the geopolymerisation process. The leaching and diffusion between particle surfaces and the gel phase may still occur, and a slight movement of paste in capillary pore may also take place.

As discussed earlier, the major difficulties in analysing geopolymer materials come from its x-ray amorphous nature and the problems in identifying all phases present at any given stage of the synthesis. As all reaction steps are taking place simultaneously, it has, so far, been too difficult to isolate each reaction step for detailed examination. If it is not possible to provide solid proof on the identification of the different phases present at each different stage, it will not be possible to formulate any convincing chemical mechanism of geopolymerisation. Thus, despite the extensive research conducted so far, there remain many areas in geopolymerisation to be explored.

It should also be noted that the chemical mechanisms discussed here are only applicable in cases where M (the alkaline metal) is either Na or K. The applicability of these chemical mechanisms to systems where M is other +1 cations (e.g. lithium) or any of the +2 cations (e.g. calcium and magnesium) is still unclear. This also leads to the novelty of the thesis, whereby the role of calcium in geopolymerisation is investigated.

With the possible precipitation of calcium silicate hydrate (CSH) gel and calcium hydroxide in a geopolymeric system, similar to the hydration of OPC, it is unclear whether calcium will actually play an identical role as sodium or potassium in the synthesis of geopolymers at ambient temperature (up to 40°C). A study therefore into
understanding the role of calcium in geopolymerisation and its importance in linking the chemistries between OPC and geopolymers will contribute to our current knowledge in geopolymerisation. Most importantly this present work will assist us in the development of geopolymers as a possible environmental friendly solution to challenges currently faced in the construction industry.

2.5 Summary and Scope of Work

From a commercial point of view, the successful introduction of geopolymer products to the construction market requires an understanding of the advantages of geopolymers over OPC, and importantly, to relate geopolymeric materials to OPC chemically and structurally. The major difference between geopolymers and OPC in terms of their chemical composition, is calcium. It is not essential for calcium to be present in a basic geopolymeric structure synthesised in a low-temperature system as described earlier in Section 2.4. The roles of sodium or potassium in geopolymerisation have been discussed extensively in the literature and it is commonly assumed that calcium will behave similarly, however this was suggested without much supporting evidence. In contrast, it is commonly acknowledged that the binding property of Portland cement is due to the formation of a colloidal calcium silicate hydrate (CSH) semicrystalline phase, as discussed earlier in Section 2.2.

Given that CSH will form when soluble calcium and silicate species are present in a neutral to mild pH environment (from OPC system to alkaline activated system) as shown earlier in Sections 2.2 and 2.3, it is thought that provided sufficient calcium is added to a geopolymeric system, a CSH based cementitious material may also result. However, the nature of this CSH product is expected to be dependent on the type and concentration of the alkaline activator present, as well as the nature and the amount of initial calcium and aluminosilicate sources used (Yip and van Deventer, 2001). Figure 2.4 shows a conceptual model of the relationship between geopolymers and OPC as proposed in the thesis. Figure 2.5 shows the proposed relationship between natural zeolite, geopolymers, alkaline activated cement and OPC.
In studying the durability of ancient construction materials in comparison to their modern counterparts, it has been demonstrated by Glukhovsky (1994) that the hydration products of ancient concrete are not limited to the hydration of ordinary Portland cement (i.e. based on the hydration of the four constituents C_3S, C_2S, C_3A and C_4AF), but also include the hydrations of low-basic alkaline or earth-earth aluminosilicate systems. This low-basic alkaline aluminosilicate system could be viewed as the basic geopolymeric systems — amorphous Na⁺ or K⁺ aluminosilicate network, commonly synthesised today. In this case, these two phases, CSH and the geopolymer phase, could coexist in a single system. However, without a detailed understanding of the relationship and interactions between these two phases, it will be difficult to proceed further in developing a new generation of concrete that possesses the durability observed in ancient concrete.

The role of calcium in ancient concrete could possibly include (1) the formation of the conventional calcium silicate hydrate (CSH), (2) participation in the geopolymerisation in forming Ca-geopolymer and, (3) bridging the bonding between the calcium silicate hydrate and geopolymers or many others. However, there is a lack of documented research involving the chemical mechanisms occurring in such systems. It is probable that both calcium silicate hydrate and geopolymers could be forming simultaneously. As a result, an investigation into the role of calcium in dictating the chemical mechanism will provide answers to the fundamental question as to whether two separate phases will be formed, or a new material will be produced instead.

In the thesis, the role of calcium in geopolymerisation will be studied in detail and it is anticipated that the form of calcium present in the matrix will determine the nature of the end products and these include the formation of a calcium-based geopolymer, alkali activated cement or ordinary Portland cement. The understanding of the role of calcium in geopolymerisation is therefore important in linking the chemistries between geopolymers and OPC as suggested earlier. Moreover, calcium is the key, which will unlock the door to the “re-discovery” of the secret behind the durability of the ancient concrete. The novelty of the thesis can therefore be summarised into three main points:
1) It is the first time that the role of calcium in geopolymers is studied in detail. The results obtained will demonstrate whether calcium will play a similar charge-balancing role as sodium and potassium in a geopolymeric structure synthesised at ambient temperature (20-30°C).

2) The chemical mechanistic relationship between ordinary Portland cement and geopolymers will be examined. This understanding is important to promote and commercialise geopolymers as a possible alternative to OPC in future research.

3) The thesis will make a significant contribution to the mechanistic understanding of geopolymerisation by proposing a chemical mechanism that describes the coexistence of a geopolymer phase and calcium silicate hydrate (CSH - a major binding phase in OPC) phase in the same system. This particular result is of major significance because it holds the key to the understanding and “re-invention” of a new concrete that matches the durability of ancient concrete.
Table 2.1: Annual production of hydraulic cement of the Top 9 cement nations and Australia for the Years 1999 to 2001 (Thousand metric tons).

<table>
<thead>
<tr>
<th>Country</th>
<th>1999</th>
<th>2000</th>
<th>2001</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>573,000</td>
<td>597,000</td>
<td>627,000</td>
</tr>
<tr>
<td>India</td>
<td>90,000</td>
<td>95,000</td>
<td>100,000</td>
</tr>
<tr>
<td>United States (including Puerto Rico)</td>
<td>87,777</td>
<td>89,510</td>
<td>90,450</td>
</tr>
<tr>
<td>Japan</td>
<td>80,120</td>
<td>81,070</td>
<td>81,000</td>
</tr>
<tr>
<td>Korea, Republic of</td>
<td>48,157</td>
<td>51,255</td>
<td>52,012</td>
</tr>
<tr>
<td>Spain (including Canary Islands)</td>
<td>35,782</td>
<td>38,115</td>
<td>40,512</td>
</tr>
<tr>
<td>Italy</td>
<td>37,299</td>
<td>38,925</td>
<td>39,804</td>
</tr>
<tr>
<td>Brazil</td>
<td>40,270</td>
<td>39,208</td>
<td>39,500</td>
</tr>
<tr>
<td>Russia</td>
<td>28,400</td>
<td>32,400</td>
<td>35,100</td>
</tr>
<tr>
<td>Australia</td>
<td>7,450</td>
<td>7,500</td>
<td>7,500</td>
</tr>
<tr>
<td>Total World Production</td>
<td>1,600,000</td>
<td>1,660,000</td>
<td>1,700,000</td>
</tr>
</tbody>
</table>
Table 2.2: Annual production of the Top 6 hydraulic cement producers in Australia for the Year 2000 (Thousand metric tons).

<table>
<thead>
<tr>
<th>Major Operating companies</th>
<th>Location of Main Facilities</th>
<th>Annual Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blue Circle Southern Cement Ltd.</td>
<td>Berrima Plant, NSW</td>
<td>1,200</td>
</tr>
<tr>
<td>Adelaide Brighton Cement Ltd.</td>
<td>Birkenhead Plant, SA</td>
<td>1,000</td>
</tr>
<tr>
<td>Cockburn Cement Ltd.</td>
<td>South Coogee Plant, WA</td>
<td>1,000</td>
</tr>
<tr>
<td>Goliath Cement Holdings Ltd.</td>
<td>Railton Plant, TAS</td>
<td>1,000</td>
</tr>
<tr>
<td>Adelaide Brighton Cement Ltd.</td>
<td>Geelong Plant, VIC</td>
<td>800</td>
</tr>
<tr>
<td>Queensland Cement Ltd.</td>
<td>Darra Plant, QLD</td>
<td>700</td>
</tr>
<tr>
<td>Total Annual Australian Production</td>
<td></td>
<td>7,500</td>
</tr>
</tbody>
</table>

Table 2.3: Typical oxide composition of a Portland cement (Gani, 1997).

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Notation</th>
<th>Common Name</th>
<th>Weight %</th>
<th>Origin From</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>C</td>
<td>Lime</td>
<td>60-67</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>SiO₂</td>
<td>S</td>
<td>Silica</td>
<td>17-25</td>
<td>Clay</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>A</td>
<td>Alumina</td>
<td>3-8</td>
<td>Clay</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>F</td>
<td>Ferric oxide</td>
<td>0.5-6</td>
<td>Clay</td>
</tr>
<tr>
<td>Na₂O, K₂O</td>
<td>N,K</td>
<td>Magnesia</td>
<td>0.5-1.3</td>
<td>Clay/Impurities</td>
</tr>
<tr>
<td>MgO</td>
<td>M</td>
<td>Alkali</td>
<td>&lt;6</td>
<td>Impurities</td>
</tr>
<tr>
<td>SO₃</td>
<td>S</td>
<td>Sulphur trioxide</td>
<td>1-3</td>
<td>Impurities</td>
</tr>
</tbody>
</table>
### Table 2.4: Typical phase mass composition and estimated heat of hydration of a Portland cement.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Chemical Composition</th>
<th>Heat of Reaction (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mass %&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Mass %&lt;sup&gt;2&lt;/sup&gt;</td>
</tr>
<tr>
<td>Alite (Tricalcium</td>
<td>3CaO.SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>50.7</td>
<td>~45</td>
</tr>
<tr>
<td>silicate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belite (Dicalcium</td>
<td>2CaO.SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>22.5</td>
<td>~25</td>
</tr>
<tr>
<td>silicate</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>3CaO.Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>8.6</td>
<td>~10</td>
</tr>
<tr>
<td>Calcium aluminoferite</td>
<td>4CaO.Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;.Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.4</td>
<td>~10</td>
</tr>
<tr>
<td>Other Phases</td>
<td></td>
<td>8.8</td>
<td>~10</td>
</tr>
</tbody>
</table>


### Table 2.5: Sequence of hydration of C<sub>3</sub>S (Barnes, 1983).

<table>
<thead>
<tr>
<th>Period</th>
<th>Reaction Stage</th>
<th>Chemical Process</th>
<th>Overall kinetic behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Early</td>
<td>I. Pre-induction period</td>
<td>Initial hydrolysis; Release of ions</td>
<td>Very rapid; Chemical control</td>
</tr>
<tr>
<td></td>
<td>II. Induction period</td>
<td>Continued dissolution; Formation of early CSH</td>
<td>Slow; Nucleation or diffusion control</td>
</tr>
<tr>
<td>Middle</td>
<td>III. Acceleration period (post-induction period)</td>
<td>Initial growth of permanent hydration products</td>
<td>Rapid; Chemical control</td>
</tr>
<tr>
<td></td>
<td>IV. Deceleration period</td>
<td>Continued growth of hydration products; Development of microstructure</td>
<td>Moderate; Chemical and diffusion control</td>
</tr>
<tr>
<td>Late</td>
<td>V. Diffusion period (steady-state period)</td>
<td>Gradual densification of microstructure</td>
<td>Very slow; Diffusion control</td>
</tr>
<tr>
<td><strong>Reaction Stage</strong></td>
<td><strong>Chemical Processes</strong></td>
<td><strong>Physical Processes</strong></td>
<td><strong>Relevance to Mechanical Properties</strong></td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------------</td>
<td>------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>First Minutes</td>
<td>Rapid initial dissolution of alkali sulphates and aluminates; initial hydration of C₃S; formation of AFt (ettringite)</td>
<td>High rate of heat evolution</td>
<td>Changes in liquid phase composition may influence the subsequent setting</td>
</tr>
<tr>
<td>First Hours (Induction Period)</td>
<td>Decrease in silicate but increase in Ca²⁺ ion concentration; formation of Ca(OH)₂ and CSH nuclei begins; Ca²⁺ concentration reaches a supersaturation level</td>
<td>Formation of any early hydration products; low rate of heat evolution; continuous increase of viscosity</td>
<td>Formation of AFt and AFm phases may influence setting and workability. Hydration of calcium silicates determines initial set end of induction period.</td>
</tr>
<tr>
<td>Approximately 3-12 hour (Acceleration Stage)</td>
<td>Rapid chemical reaction of C₃S to form CSH and Ca(OH)₂; decrease of Ca²⁺ supersaturation</td>
<td>Rapid formation of hydrates leads to solidification and decrease in porosity; high rate of heat evolution</td>
<td>Change from plastic rigid consistency (initial and final set); early strength development.</td>
</tr>
<tr>
<td>Component</td>
<td>Approx. volume %</td>
<td>Specific gravity</td>
<td>Typical morphology</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>------------------</td>
<td>------------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>Calcium silicate hydrate (CSH)</td>
<td>50</td>
<td>2.1-2.6</td>
<td>Variable</td>
</tr>
<tr>
<td>Calcium hydroxide (CH)</td>
<td>12</td>
<td>2.24</td>
<td>Equant crystals</td>
</tr>
<tr>
<td>Ettringite (AFt)</td>
<td>13*</td>
<td>~1.75</td>
<td>Prismatic needles</td>
</tr>
<tr>
<td>Calcium monosulphoaluminate hydrate (AFm)</td>
<td>13*</td>
<td>~1.95</td>
<td>Hexagonal platelets or irregular “rosettes”</td>
</tr>
<tr>
<td>Pores</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
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<td></td>
</tr>
</tbody>
</table>

* The total amount of AFt and AFm combined
<table>
<thead>
<tr>
<th>Category</th>
<th>Structure</th>
<th>Alkali cation</th>
<th>Utilisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polysialate (PS)</td>
<td>$M_n^- (\text{Si-O-Al-O}_n)$</td>
<td>K-PS</td>
<td>Thermal</td>
</tr>
<tr>
<td></td>
<td>$\bigcirc \bigcirc$</td>
<td>Na-PS</td>
<td>insulation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-PSS</td>
<td>Refractory</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Na-PSS</td>
<td>Fire-resistant</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K,Ca-PSS</td>
<td>Performance cement</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Toxic waste</td>
</tr>
<tr>
<td>Polysialate-siloxo (PSS)</td>
<td>$M_n^- (\text{Si-O-Al-O-Si-O}_n)$</td>
<td>K-PSS</td>
<td>Tooling</td>
</tr>
<tr>
<td></td>
<td>$\bigcirc \bigcirc \bigcirc$</td>
<td>Na-PSS</td>
<td>composites</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F,K,Na-PSDS</td>
<td>Refractory</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K-PSDS</td>
<td>Fire-resistant</td>
</tr>
<tr>
<td>Polysialate-disiloxo (PSDS)</td>
<td>$M_n^- (\text{Si-O-Al-O-Si-O-Si-O}_n)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\bigcirc \bigcirc \bigcirc \bigcirc$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 2.9: The comparison between the synthesis of zeolites and geopolymers
(Xu, 2002).

<table>
<thead>
<tr>
<th></th>
<th>Zeolite</th>
<th>Geopolymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactants</td>
<td>Al complexes solution + Si complexes solution</td>
<td>Aluminosilicate source material + alkaline solution + silicates (solid/liquid)</td>
</tr>
<tr>
<td>Early stage of reaction</td>
<td>Nucleation in solution</td>
<td>Leaching of aluminosilicate solid into paste</td>
</tr>
<tr>
<td>Later stage of reaction</td>
<td>Crystal growth in solution</td>
<td>Diffusion and condensation of leached Al and Si complexes in paste</td>
</tr>
<tr>
<td>Temperature</td>
<td>90 - 300°C</td>
<td>Ambient</td>
</tr>
<tr>
<td>pH</td>
<td>6 – 11</td>
<td>14</td>
</tr>
<tr>
<td>Product</td>
<td>Crystalline zeolite</td>
<td>Mixture of gel and aluminosilicate solid source materials</td>
</tr>
<tr>
<td>Composition</td>
<td>Certain stoichiometric formula</td>
<td>No certain stoichiometric composition</td>
</tr>
<tr>
<td>Structure</td>
<td>Unique crystal</td>
<td>Mixture of amorphous to semicrystalline gel phase and crystalline aluminosilicate source materials</td>
</tr>
<tr>
<td>Mechanical strength</td>
<td>Low</td>
<td>High</td>
</tr>
</tbody>
</table>
Figure 2.1: Schematic view of cement production (Jackson and Dhir, 1996).
Figure 2.2: Basic structure of calcium silicate hydrate (Faucon et al., 1998a, b).

Figure 2.3: Proposed three-dimensional structure of metakaolin-based geopolymer (Davidovits, 1994a).
Figure 2.4: Conceptual model of the relationship between geopolymers and ordinary Portland cement.
Figure 2.5 Conceptual model of the relationship between natural zeolites, geopolymers, alkali activated cement and ordinary Portland cement.

(Note: Alkaline activated cement consists of a range of systems, including alkaline activated flyash and alkaline activated slag, in which the alkaline activated slag relates more closely to the OPC system and alkaline activated flyash relates more closely to the geopolymeric system. The exact relationship is dependent on the mineralogy of the raw material.)
Chapter 3

Experimental and Research Methods

This chapter will describe the different raw materials including, the aluminosilicate source, calcium source and alkaline activator used in this research. It will also characterise all the calcium sources used in the thesis, which include industrially processed calcium material (e.g. ground granulated blast furnace slag), natural mineral (e.g. wollastonite - calcium silicate) and analytical grade chemical (e.g. calcium hydroxide). The use of a wide range of experimental techniques and methods in this study is necessary in order to examine the microscopic and macroscopic features of the resultant product, and most importantly, to understand the mechanistic effect of the different chemical sources on geopolymerisation.

This chapter will also describe and provide a fundamental background on the main techniques and experimental methods used in the study, which include x-ray diffraction (XRD), x-ray fluorescence (XRF), inductively coupled plasma optical emission spectroscopy (ICP-OES), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive x-ray spectroscopy (EDS), specific surface area and particle size analysis, compressive strength tests and leaching tests.

3.1 Raw Materials

3.1.1 Aluminosilicate Source
The alkaline activation of an aluminosilicate source will give rise to a three dimensional aluminosilicate network, which is also the major binding phase in the formation of a geopolymeric gel (Lee and van Deventer, 2002; Alonso and Palomo,
2001a; Phair and van Deventer, 2001; van Jaarsveld, 2000; Xu and van Deventer, 2000; Davidovits, 1999; Krivenko, 1994). The choice of a suitable aluminosilicate source which is free of calcium in the present work is important because it will simplify the investigation by assuming all calcium ions detected in the resultant binder originated from the calcium sources added. It is therefore possible to elucidate the mechanistic path of calcium in the reactions occurring in the geopolymer system. Moreover, the aluminosilicate used in the investigation must be able to undergo geopolymerisation rapidly in an alkaline activator. Subsequently, with the addition of a calcium source, it is possible to investigate how the calcium affects the system macroscopically and microscopically, in which geopolymeric gel is the major binding phase in the absence of any calcium material.

Different types of aluminosilicate sources have been studied and investigated at the initial stage of the investigation and they include: kaolin, metakaolin, fire clay, ball clay, calcined flint clay, mullite, feldspar and flyash. Table 3.1 shows the oxide composition of all these materials as determined by x-ray fluorescence (XRF), using a Siemens SRS 3000 instrument.

Kaolin, feldspar and flyash have been studied extensively by various researchers as possible aluminosilicate sources in geopolymerisation (Phair and van Deventer, 2001; Lee and van Deventer, 2000; Xu and van Deventer, 2000; Palomo et al., 1999a). However, they all fail to satisfy both criteria as discussed earlier, namely: (1) free of calcium and (2) sufficiently reactive to the alkaline activator. From Table 3.1, it can be seen that the two fly ashes available contain too much calcium (>3 wt.%), and more importantly, the calcium in the fly ashes is likely to be associated with a number of different calcium containing glassy phases. The current knowledge of understanding the reactivity of each calcium phase is still limited; subsequently the use of flyash as the possible aluminosilicate source in the thesis will make the investigation difficult. In the case of kaolin and feldspar, although they contain virtually no calcium in their composition, these two natural minerals do not undergo geopolymerisation rapidly enough. It is therefore impossible to have a clear picture on how the presence of calcium would affect geopolymerisation. Fire clay, ball clay, calcined flint clay and mullite have been used vastly in the manufacturing of ceramics, however, they were found to be unsuitable as the main source of aluminosilicate, due to their poor
reactivity. Metakaolin (calcined kaolin) was the only material found to satisfy the two requirements, and hence was chosen to be the main source of aluminosilicate in the present work.

3.1.1.1 Metakaolin

Metakaolin (MK) is an amorphous source of aluminosilicate material, which is produced by the calcination of clay (kaolin). The crystalline aluminosilicate structure of kaolin is destroyed by heating to 700-800°C during the calcination process. MK has been used extensively as the aluminosilicate source in the synthesis of geopolymers (Alonso and Palomo, 2001a, b; Phair and van Deventer, 2001; Granizo et al., 2000; Krivenko et al., 1999; Silva et al., 1999; Palomo and Glasser, 1992). It has also been widely used as a mineral admixture in the manufacturing of cementitious materials (Asbridge et al., 2002; Bai et al., 2002; Frias and Cabrera, 2001, 2000; Qian and Li, 2001; Roy et al., 2001; Coleman and McWhinnie, 2000; Frias et al., 2000; Ramlochan et al., 2000; Coleman and Page, 1997; Wild et al., 1996; Atkins et al., 1995; Zhang and Malhotra, 1995; Ambroise et al., 1985; Murat, 1983a, b; Murat and Comel, 1983), and in the synthesis of zeolites (Akolekar et al., 1997; Atkins et al., 1995; Murat et al., 1992; Madani et al., 1990). The synthesis of metakaolin from kaolin has also been studied in great detail (Madani et al., 1990; Newman, 1987).

MK used in the thesis is a commercially available MK obtained from ECC International under the brand name of MetaStar 402 (particle size 99% <20μm). As a result of purification before calcination, MetaStar 402 contained less than <0.1% CaO (Table 3.1). In the thesis it has therefore been assumed that all calcium found in the geopolymeric product originated from the calcium source used in the investigation.

3.1.2 Calcium Source

A total of ten calcium materials have been used in the synthesis of geopolymers in the present work, and various types of calcium salts (AR grade) have been used as the calcium standard in a number of studies throughout the thesis. The calcium materials used can be grouped into two main categories: (1) industrially processed calcium materials, and (2) natural minerals. Two processed calcium materials (ground granulated blast furnace slag (GGBFS) and cement) and eight other natural minerals
are used in total. Amongst the eight natural calcium minerals used, they can be further classified into three main classes based on the anionic part of the minerals, which include: silicate, carbonate and sulphate. These ten materials cover a range of elemental composition, mineralogy, crystal structure and also pre-treatment history. The oxide compositions of all calcium silicate sources and other calcium sources used are shown in Tables 3.2 and 3.3 respectively.

A detailed discussion of the effects of the chemical, physical and mineralogical properties of these calcium sources and their subsequent impact on geopolymerisation can be found in the different chapters presented. The following section will only describe and characterise all the calcium sources used.

3.1.2.1 Industrially Processed Calcium Material
Two processed calcium materials are used in the current work and they are ground granulated blast furnace slag (GGBFS) and ordinary Portland cement (OPC), with GGBFS being the principal calcium source used in the investigation. GGBFS was obtained from Independent Cement P/L, Melbourne, Australia. OPC was obtained from Geelong Cement Limited, Australia.

GGBFS is a by-product of the manufacture of iron in the blast furnace and is essentially an amorphous source of calcium silicate. This waste results from the fusion of lime, arriving from the limestone added to the furnace, with the siliceous and aluminous residues from the iron ore and from the coke used for its reduction (Jackson and Dhir, 1996). From XRD analysis, gypsum (calcium sulphate dihydrate, CaSO₄.2H₂O) is the only major crystalline phase found in the GGBFS used in the thesis.

Cement contains several crystalline and semi-crystalline phases, which includes various forms of calcium silicate and calcium aluminate. The manufacturing process and the properties of OPC have been described in Chapter 2. Both cement and GGBFS were subjected to thermal or calcination treatment in their respective manufacturing processes. It is thought the history of these minerals will have a significant impact on their efficiency in participating in the geopolymerisation reaction.
3.1.2.2 Natural Calcium Mineral

The eight natural calcium minerals used in the study cover three different classes of minerals based on the anionic part of the mineral and they are silicate (wollastonite, prehnite, hornblende, tremolite, and anorthite calcium plagioclase), carbonate (calcite and dolomite) and sulphate (bassanite). These minerals also cover a range of elemental composition, crystal structure and mineralogy. The detailed physical properties and mineralogy of each of the minerals used are presented in Table 3.4.

Wollastonite (calcium silicate, CaSiO₃), calcite (calcium carbonate, CaCO₃) and dolomite (calcium magnesium carbonate, CaMgCO₄) were purchased from Claywork, Melbourne, Australia. Bassanite (calcium sulphate hemihydrate, CaSO₄·0.5H₂O) used in the study was manufactured by CSR Ltd, under the product name of Gyprock Base Coat 100. This material is categorised as a plaster based cement and adhesive, and is commercially used as a gypsum plaster based setting type cement for joining plasterboard to masonry and concrete surfaces. All other calcium minerals were purchased from Geological Specimen Supplies, Turramurra, Australia. These calcium minerals came at an approximate size of 5 cm x 5cm x 5cm. After being crushed, they were ground and sieved to ~67μm.

It is thought the different mineralogy of the calcium sources will have a significant effect on the extent of dissolution in an alkaline medium, and subsequently, the reactivity of the calcium materials in a geopolymeric system. The interrelationship between the mineralogy and reactivity of different calcium materials has a significant influence on how each of them will participate in geopolymerisation. It is anticipated that the physical properties of the resultant products are dependent on the nature of the starting materials and the interactions between the different phases will hold the key to the durability of the resultant binders.

3.1.3 Other Materials

Fine washed sand (100% <2mm) obtained from Commercial Minerals, Australia, was used as the aggregate in the synthesis of mortars that were subjected to compressive strength testing. Samples subjected to other analysis were prepared without the addition of the washed sand.
Silica fume obtained from Simcoa's silicon plant, Australia, was used as a pure silica (SiO$_4$) source in a number of experiments in the investigation. Analytical grade aluminium hydroxide powder (Merck P/L, Australia) and aluminium oxide (Merck P/L, Australia) were also used throughout the investigation as the aluminium standard.

Analytical grade calcium oxide (CaO), calcium hydroxide (Ca(OH)$_2$), calcium carbonate (CaCO$_3$) were used throughout the investigation as the calcium standard. The calcium carbonate powder was manufactured by BDH Laboratory Supplies, England. Both calcium oxide powder and calcium hydroxide were supplied by Merck P/L, Australia.

Sodium hydroxide, sodium silicate and distilled water were used to make the alkaline activator required in the synthesis of geopolymers. The sodium silicate solution used in experiments was supplied by PQ Australia Pty. Ltd, under the brand name of Vitrosol N48 (28.7% SiO$_2$, 8.9% Na$_2$O and 62.4% H$_2$O; density 1370kg/m$^3$). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia.

The effect of chelating agent addition was one of the aspects investigated in the current work. Ethylenediaminetetraacetic acid (EDTA) disodium salt and sodium oxalate were used as the main chelating agents and they were both supplied by Merck P/L, Australia. The Elemental Standards used in the ICP analysis, as discussed later in this chapter were manufactured by EM Industries, US.

### 3.2 Synthesis of Geopolymeric Samples

Geopolymers were prepared by mixing metakaolin (MK) with or without the addition of calcium sources (CA) in an alkaline activator (sodium hydroxide NaOH + sodium silicate NaSi) solution. Three different sets of alkaline activators were prepared at different alkalinity (Ms = SiO$_2$/Na$_2$O molar ratio = 2.0, 1.5 and 1.2). The mass ratio between total mass of the dry raw material (MK + CA) and the alkaline activator used was 0.69, 0.65, 0.61 for Ms = 2.0, 1.5 and 1.2 respectively. These ratios were selected
in order to maintain consistent water and soluble silicate content in all binders with the amount of sodium hydroxide added being the only variable.

To make the alkaline activator, sodium hydroxide pearl was mixed with a sodium silicate solution to form an alkaline solution with three different molar ratios (Ms = 2.0, 1.5 and 1.2). The hot solution was then cooled overnight to ambient temperature. Samples were synthesised using a mass ratio between MK and the calcium source (CA), ranging from MK/(MK + CA) = 0 to 1. The mass ratio between the dry mix (MK and CA) and the alkaline mix (NaOH + NaSi) remains constant for a particular alkaline (Ms) condition regardless of the ratio between MK/(MK + CA) used.

MK and CA were mixed thoroughly at a specified ratio until a uniform mix was produced. The alkaline activator solution was subsequently stirred into the dry mix to form a paste. The paste was mixed for a further 3 minutes. The paste was then poured into PVC cylindrical moulds (50mm diameter and 100mm length) and allowed to cure in a laboratory convection oven at 40°C for 24 h before being extracted from the moulds and hardened at room temperature (25°C) prior to testing at specified times. For binders subjected to compressive strength testing, washed sand (with mass ratio = sand/(MK + CA) = 3) was gradually added to the homogeneous paste until a uniform mixture was formed before pouring into the mould as described. All samples were cured at atmospheric pressure and no attempt was made to control the humidity during curing.

3.3 Leaching test

Leaching tests were used to determine the leachability of Si, Al, Ca, Mg and Fe from all the raw materials used. This will allow an in-depth examination on the dissolution step, which is commonly believed to be the first step of geopolymerisation. Moreover, the leaching test can be used to correlate the chemical, physical and mineralogical properties of the different sources with their leachability and their subsequent impact on geopolymerisation.
Suspensions containing 50g of solid in 100mL alkaline solution were prepared using different concentrations of sodium hydroxide (2.5, 5 and 7.5M). Suspensions were mixed for 1, 2, 4, 8 and 24h before centrifuging, filtration and dilution with 10% conc. HCl before analysing elemental concentrations of Si, Al, Ca, Mg and Fe by ICP-OES (Perkin-Elmer 3000). The liquid obtained after centrifugation was filtered through a 0.2μm Minisart® membrane filter (Sartorius AG Germany) to further remove the suspended solid. The conditions used for the dissolution work should be similar to those used in normal geopolymer synthesis. However, due to the complexity of the reactions that occur when soluble alkali silicate is added to metakaolin, no soluble silicate source was added to the current dissolution work. The NaOH concentration of 2.5M, 5M and 7.5M used in the leaching experiment closely resembled the alkalinity in the synthesis of matrices under Ms = 2.0, 1.5 and 1.2 respectively.

3.4 Characteristics of Raw Materials and Geopolymeric Specimens

3.4.1 X-Ray Fluorescence (XRF) Analysis

XRF is used to analyse the elemental composition of all the raw materials used in the thesis. A Siemens SRS3000 sequential XRF spectrophotometer is capable of measuring elements above atomic number 8 with a detection limit typically of the order of 5ppm with the counting schemes in place. A wide range of spec-pure reagents and certified reference standards allow for thorough characterisation of any unknown sample. Loss on ignition is determined by fusion. Figure 3.1 shows a photo of the Siemens SRS3000 sequential XRF spectrophotometer used in this investigation.

Each sample powder (3-4g) was heated in a ceramic crucible at 105°C for at least 2-3 hours (preferably overnight). The sample was then removed from the oven and the crucible covered with a watch glass and allowed to cool to room temperature. Precisely 1.000g of sample powder was added into vials containing 5.000g of lithium metaborate (LiBO2) powder, which was pre-dried overnight in a furnace at 500°C. Approximately 0.5g ammonium nitrate (to oxidise sulphides) was then added to each vial and homogenised by shaking vigorously. Platinum crucibles were pre-weighed and the content of each vial was added to separate crucibles. The platinum crucibles were then preheated in a furnace (600°C) for 5-10 minutes, or until all brown vapours
from ammonium nitrate were expelled. The furnace temperature was then increased to 900ºC in order to melt each sample for 5-10 minutes. Each crucible was then removed from the furnace, and transferred to stand and heat over a Meker burner. Each sample was heated until there was no undissolved particles remaining. The crucible was then removed from the heat and after cooling to room temperature, the crucible was weighed to determine the weight of glass after fusion. The glass was then re-melted at about 1000ºC. The melted samples were then poured into graphite moulds. Each sample was removed out of its mould after about 20 minutes for annealing overnight.

The glass discs for XRF analysis were prepared using a steel file to knock off excess glass from edges. The disc was then polished with fine silicon carbide polishing powder and on a glass plate with fine corundum powder. The glass was then washed immediately under a high pressure tap and pad dried with tissue paper before putting it into the steel sample holder and subjected to XRF analysis.

In the special case of a sulphide rich sample (e.g. calcium sulphate hemihydrate – the bassanite studied in the thesis), a different preparation method was required. In general, the standard fusion method does not apply to specimens with more than 5% sulphides. If the sulphide content is between 1-5%, the sample must be oxidised using ammonium nitrate for a much longer time.

3.4.2 X-Ray Diffraction (XRD) Analysis

XRD is routinely used for the identification of the mineralogical composition of dry powder samples. In the thesis, raw materials and resultant products were mechanically ground by a ring mill and analysed by XRD. XRD analysis was performed on random powder mounts utilising a Philips PW 1800 diffractometer with CuKα radiation (characteristic wavelength 0.1542nm) generated at 20 mA and 40kV. The XRD patterns were recorded on a Phillips PW1800 machine, which has a fully integrated automatic powder diffraction that consists of a high speed, high precision goniometer, high efficiency generator and automatic sample loading facility. A scanning rate of 2°/min from 5 to 70° 2-theta was used to give the structural information of each specimen studied. Figure 3.2 shows a photo of the Philips PW 1800 diffractometer used in this investigation.
The obtained patterns were characterised using a computer program XPLoT™ and identified by comparing the diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data, in which, a list of measured d-spacings for the sample are compared to standard line patterns supplied annually by the International Centre for Diffraction Data (ICDD).

3.4.3 Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

The elemental compositions of the leached solutions obtained from dissolution tests (Section 3.3), were analysed by a Perkin Elmer Optima 3000 Inductively Coupled Plasma Spectrometer (ICP-OES) containing an argon plasma arc. Figure 3.3 shows a photo of the Perkin Elmer Optima 3000 instrument used in this investigation.

It was discussed previously by Phair (2001) that special emphasis must be placed on utilisation of the ICP-OES for the analysis of silicon in solution including colloidal silica. It was found that an error in total silicon detection occurred above 100 ppm particularly in acidic solution, which causes silicate to precipitate as a gel in the base of test tubes, making it undetectable by analysis (Phair, 2001). Subsequently, all solutions analysed in the thesis were diluted to ensure the samples undergoing analysis had less than 100 mg/L Si (to prevent spontaneous polymerisation) as suggested by Phair (2001). This will also ensure that there will be less than 200 mg/L Na present in the solution. Moreover, each sample solution was further diluted with a 10% concentrated HCl solution, to ensure all dissolved species remained in solution.

For each reading, two spectral lines of each element were used to determine the elemental composition. The spectral lines used were: calcium 317.933nm and 315.887nm; silicon 251.611nm and 212.412nm; aluminium 308.215nm and 309.271nm; iron 238.204nm and 239.562nm; magnesium 285.213nm and 279.077nm. A linear calibration curve was established from the blank and standard solutions of elemental concentrations similar to those to be used in the experiment under the same alkalinity. The argon arc was calibrated against a mercury lamp before each analysis to ensure the optimum performance of the machine. The Optima 3000™ software package was used in the operation of the machine, and this software was used to calibrate the peak line intensity against concentration (mg/L) automatically.

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3.4.4 Scanning Electron Microscopy (SEM), Backscattered Electron Microscopy (BEM) and Energy Dispersive X-ray Spectroscopy (EDS)

SEM and SEM/EDS are the key techniques used in the thesis. The main purpose of SEM is to provide information on the morphology and composition of the surface of all raw materials as well as the binder synthesised. Moreover, SEM/EDX can be used to analyse the elemental composition of each micro-phase present in the structure. The microanalysis of the material before and after the reaction will provide a physical description of the microstructure of the binder synthesised, which could not be described successfully using other techniques.

Two different scanning electron microscopes were used in the investigation and they were: A JEOL JSM-840 microscope with Tracor Northern EDAX system, and a Phillips XL30 SEM coupled with an Oxford energy dispersive spectrometer. Both microscopes were operating at the accelerating voltage of 20kV. The JEOL machine was used for the SEM and EDX elemental analysis, while the Philips was used for the SEM and BEM (backscattered electron microscopy) as well as the EDX elemental analysis.

The sample preparation for both SEM and SEM/EDS was identical. Samples for analysis were either mounted randomly as a powder, or mounted as thin section. Since geopolymers are poor electrical conductors, the samples have to be gold coated (for image analysis) or carbon (for elemental analysis) coated before analysis to ensure the surface of the sample is conductive. The microscopic analysis under SEM can only be conducted on electrically conductive samples. Each sample was therefore placed on sample holders that were supported by a carbon conductive paint. The sample coating was then performed on a DYNAVAC sputter coater, which evaporated carbon (or gold) onto the sample.

Apart from providing vital information regarding the elemental composition of the sample through the EDS analysis on the sample surface, the optical contrast on the scanning electron micrograph and backscattering electron micrograph will also provide useful material information, in which the intensity of reflected electrons is proportional to the atomic number of the elements in the object as well as the density.
of the material (Andac and Glasser, 1998). In most cases, the difference in the optical contrast in the different region of the microstructure is a first indication of the presence of different components in the binder. This will be discussed further in the relevant parts of the thesis.

3.4.5 Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) and Electron Diffraction

TEM is a powerful technique to identify crystalline particles, as well as semi-crystalline and amorphous particles in the structure. A Philips EM420 transmission electron microscope with an EDAX PV 9900 energy dispersive x-ray microanalyser operating at the accelerating voltage of 100kV was used in the study. The transmission electron micrographs were taken to show the morphology of the particles in a sub-micron scale, while the further electron diffraction analysis conducted on the particle was used to study crystal structure of the particle of interest. The advantage of electron diffraction over x-ray diffraction is that it enables the study of amorphous phases.

In general, specimen preparation for TEM requires that sample materials be thinned so as to become transparent to the electron beam and this usually requires the thickness to be approximately ~ 100nm. For electrically conductive material, this can usually be achieved by electrolytic polishing, in which a thin disc of material is electrolytically dissolved to leave a high specula finish. When the disc is perforated, the regions in the vicinity of the hold are usually thin enough for electron transparency.

However, since geopolymers are poor electrical conductors, this standard method could not be used. Instead, the sample preparation for the TEM analysis in this thesis consisted of bulk grinding the sample in ethanol in an agate mortar. The ethanol containing the suspended particles was then transferred onto amorphous carbon covered copper grids where the ethanol was left to evaporate, leaving a layer of very fine particles on an amorphous carbon film. The size range of particles analysed was approximately 500 to 1000nm, so that the adsorption of fluorescence and x-ray from specimen can be neglected (Xu, 2002).
3.4.6 Surface Area and Particle Size Analysis

The particle size distribution and the estimation of the surface area for all raw materials used were determined using a Coulter LS130 optical particle size analyser. Particles were introduced in an aqueous suspension of distilled water to give a concentration of roughly 1% by mass.

3.4.7 Compressive Strength Testing

Compressive strength testing was performed as per Australian Standard (AS1012.9-1999) using three 50mm diameter cylinders with a 1:2 diameter to length ratio. The top face of the cylinder was cut parallel to the bottom face by using a diamond saw prior to the compressive strength testing. The top surface of the sample was capped with fast setting Boral Dental Plaster (a gypsum plaster) to ensure the diameter and length ratio remained at 1:2 and to create accurate perpendicular surfaces on both side of the test cylinder preceded the testing. The plaster was then left to dry at room temperature and atmospheric pressure for at least 3h, prior to testing for compressive strength. All compressive strength measurements were taken as the average of strength results of three samples. An ELE International Auto Test Compression Machine using a pace rate of 1kNs⁻¹ was used for testing after 1, 7, 28, 90, 180, 240, 360, 540 and 720 days of synthesis. Figure 3.4 shows a photo of the machine used.

3.5 Summary

An overview of all raw materials, as well as the experimental methods used in the thesis has been presented in this chapter. Most of the techniques presented here are the most commonly used techniques in materials science to characterise material, or monitoring the chemical reactions/changes taking place in any given system. Further information on the raw materials and the analysis techniques applied will be presented in the relevant sections of the thesis.
Table 3.1 Composition of all aluminosilicate sources used as determined by XRF analysis (mass%).

<table>
<thead>
<tr>
<th>Element as Oxide</th>
<th>Meta-kaolin&lt;sup&gt;1&lt;/sup&gt; (HR1F)</th>
<th>Kaolin (Eckglas)</th>
<th>Fire Clay</th>
<th>Ball Clay</th>
<th>Calcined Flint Clay</th>
<th>Flyash (Gladstone)&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Flyash (PA)&lt;sup&gt;3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>0.1</td>
<td>0.2</td>
<td>0.05</td>
<td>0.13</td>
<td>0.03</td>
<td>0.2</td>
<td>3.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>54.78</td>
<td>54.5</td>
<td>49</td>
<td>70.3</td>
<td>57.8</td>
<td>50.6</td>
<td>50.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>40.42</td>
<td>29.4</td>
<td>37</td>
<td>23.6</td>
<td>26.8</td>
<td>46.5</td>
<td>28.0</td>
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<tr>
<td>Fe₂O₃</td>
<td>0.76</td>
<td>1.4</td>
<td>0.83</td>
<td>1.02</td>
<td>1.1</td>
<td>0.8</td>
<td>12.0</td>
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<tr>
<td>MgO</td>
<td>0.42</td>
<td>0.2</td>
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<td>0.51</td>
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<td>K₂O</td>
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<td>TiO₂</td>
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<td>SO₃</td>
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<td>-</td>
<td>-</td>
<td>-</td>
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<td>LOI</td>
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<td>11</td>
<td>11.9</td>
<td>0.32</td>
<td>8.2</td>
<td>0.7</td>
<td>2.0</td>
</tr>
</tbody>
</table>

1 Commercially available metakaolin, MetaStar 402, manufactured by ECC International, UK.
2 Gladstone Flyash, obtained from Gladstone Power Station in Australia.
3 Port Augusta (PA) Flyash, obtained from Port Augusta Power Station in Australia.
Table 3.2 Composition of all calcium silicate sources used as determined by XRF analysis (mass%).

<table>
<thead>
<tr>
<th>Element as Oxide</th>
<th>Industrial Processed Materials</th>
<th>Natural Minerals</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Granulated Blast Furnace Slag</td>
<td>Wollastonite</td>
<td>Anorthite Plagioclase</td>
</tr>
<tr>
<td>CaO</td>
<td>43</td>
<td>47.5</td>
<td>15.43</td>
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<tr>
<td>SiO₂</td>
<td>34.4</td>
<td>50.5</td>
<td>47.38</td>
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<td>Al₂O₃</td>
<td>14.1</td>
<td>0.25</td>
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<td>Fe₂O₃</td>
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<td>0.2</td>
<td>0.84</td>
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<td>MgO</td>
<td>6.3</td>
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<td>1.42</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.3</td>
<td>0.3</td>
<td>1.26</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.33</td>
<td>0.33</td>
<td>0.57</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.96</td>
<td>0.11</td>
<td>0.06</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.45</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>LOI</td>
<td>0.05</td>
<td>0.54</td>
<td>1.99</td>
</tr>
</tbody>
</table>

Table 3.3 Composition of the calcium carbonate and calcium sulphate sources used as determined by XRF analysis (mass%).

<table>
<thead>
<tr>
<th>Element as Oxide</th>
<th>Calcite</th>
<th>Dolomite</th>
<th>Bassanite (Calcium sulphate hemihydrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>53.54</td>
<td>33.4</td>
<td>37.88</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.48</td>
<td>2.5</td>
<td>5.18</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.34</td>
<td>0.7</td>
<td>1.91</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.21</td>
<td>0.3</td>
<td>0.32</td>
</tr>
<tr>
<td>MgO</td>
<td>1.65</td>
<td>17.1</td>
<td>0.67</td>
</tr>
<tr>
<td>Na₂O</td>
<td>-</td>
<td>0.1</td>
<td>0.38</td>
</tr>
<tr>
<td>K₂O</td>
<td>-</td>
<td>0.1</td>
<td>0.47</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02</td>
<td>0.05</td>
<td>0.09</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>-</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>SO₃</td>
<td>-</td>
<td>-</td>
<td>32.04</td>
</tr>
<tr>
<td>LOI</td>
<td>42.75</td>
<td>45.75</td>
<td>15.94</td>
</tr>
</tbody>
</table>
Table 3.4: Physical properties of calcium source (CA) materials. (Crystallinity: A = amorphous, B = semi-crystalline and C = crystalline).

<table>
<thead>
<tr>
<th>Material</th>
<th>CA</th>
<th>Crystallinity</th>
<th>Mineral Group</th>
<th>Silicate Group</th>
<th>Crystal System</th>
<th>Ideal Stoichiometry</th>
<th>Hardness (Mohs)&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Density (g/cm&lt;sup&gt;3&lt;/sup&gt;)&lt;sup&gt;1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground granulated blast furnace slag Cement Wollastonite</td>
<td>GGBFS</td>
<td>A</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cement Wollastonite</td>
<td>CEM WOL</td>
<td>B,C</td>
<td>C</td>
<td>Silicate - Wollastonite</td>
<td>Triclinic</td>
<td>CaSiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4.8</td>
<td>2.92</td>
</tr>
<tr>
<td>Anorthite calcium plagioclase Hornblende</td>
<td>ANO HRN</td>
<td>C</td>
<td>C</td>
<td>Silicate - Feldspar</td>
<td>Triclinic</td>
<td>CaAlSi&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;8&lt;/sub&gt;</td>
<td>6.3</td>
<td>2.76</td>
</tr>
<tr>
<td>Prehnite</td>
<td>PRH</td>
<td>C</td>
<td>C</td>
<td>Silicate - Phyllosilicates</td>
<td>Orthorhombic</td>
<td>(Ca&lt;sub&gt;2&lt;/sub&gt;Na&lt;sub&gt;2&lt;/sub&gt;)(Mg&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;2+&lt;/sup&gt;Fe&lt;sup&gt;3+&lt;/sup&gt;Al&lt;sub&gt;3&lt;/sub&gt;)(Al,Si&lt;sub&gt;6&lt;/sub&gt;O&lt;sub&gt;22&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>5.5</td>
<td>3.24</td>
</tr>
<tr>
<td>Tremolite</td>
<td>TRM</td>
<td>C</td>
<td>C</td>
<td>Carbonate</td>
<td>Orthorhombic</td>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;Si&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;10&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.93</td>
<td>6.3</td>
</tr>
<tr>
<td>Calcite</td>
<td>CAL</td>
<td>C</td>
<td>C</td>
<td>Carbonate - Inosilicates</td>
<td>Monoclinic</td>
<td>Ca&lt;sub&gt;2&lt;/sub&gt;MgsSi&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;22&lt;/sub&gt;(OH)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Dolomite</td>
<td>DOL</td>
<td>C</td>
<td>C</td>
<td>Carbonate</td>
<td>Rhombohedral</td>
<td>CaCO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>Bassanite</td>
<td>HEM</td>
<td>C</td>
<td>C</td>
<td>Sulphate</td>
<td>Monoclinic</td>
<td>CaMg(CO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3.5</td>
<td>2.87</td>
</tr>
</tbody>
</table>

1 CRC Handbook of Chemistry and Physics, 2000
Figure 3.1 Siemens SRS3000 sequential x-ray fluorescence (XRF) spectrometer.

Figure 3.2 Philips PW1800 x-ray diffraction (XRD) spectrometer using a Cu K$^\alpha$ anticathode.
Figure 3.3 Perkin-Elmer 3000 inductively coupled plasma optical emission spectrometer (ICP-OES).
Figure 3.4 ELE International Auto Test compression machine.
Chapter 4

Effect of Ground Granulated Blast Furnace Slag (GGBFS) on Geopolymerisation

Chapter 2 proposed that the poor understanding of the role of calcium in geopolymerisation and the link between the chemistries of geopolymers and ordinary Portland cement (OPC), is likely to have inhibited the possible formation of a modern concrete that will match the durability of ancient concrete. This chapter examines the physical and chemical mechanistic effects of ground granulated blast furnace slag (GGBFS) on geopolymerisation through a range of analytical techniques including compressive strength testing, x-ray diffraction and electron microscopy. GGBFS, an amorphous source of calcium silicate, is chosen as the chief calcium source studied in the thesis because it is currently used in the construction industry as a replacement for ordinary Portland cement (OPC). Moreover, it is a waste material generated in a large quantity from the iron industry each year. The utilisation of GGBFS in the production of a novel construction material will therefore be beneficial to the environment.

This chapter establishes that it is possible to form a geopolymeric gel and a calcium silicate hydrate (CSH) gel simultaneously within a single binder. The coexistence of these two separate phases is dependent on the alkalinity of the alkaline activator and the mass ratio between the metakaolin (MK) and GGBFS used. The formation of CSH gel together with the geopolymeric gel takes place only when a low concentration of NaOH is used. In the presence of high concentrations of NaOH (molarity >7.5M), the geopolymeric structure has been found to be the dominant phase formed with the scattering of small calcium precipitates situated within the binder. The coexistence of the two phases is not observed unless a substantial amount of calcium source is present initially. It is anticipated that voids and pores within the geopolymeric binder are filled with the CSH gel, which helps to bridge the gaps
between the different hydrated phases and unreacted particles, resulting in the observed increase in mechanical strength.

*(The work presented in this chapter is based on the manuscript: C.K. Yip, G.C. Lukey and J.S.J. van Deventer, "The Coexistence of Geopolymeric Gel and Calcium Silicate Hydrate at the Early Stage of Alkaline Activation," Cement and Concrete Research, accepted 2004).*

### 4.1 Background

#### 4.1.1 Introduction

The search for a new environmentally friendly construction material that will match the durability of ancient concrete has motivated the study of alkaline activated cementitious systems since the 1950s. Alkaline activated cements refer to any system that uses an alkaline activator to initiate a reaction or a series of reactions that will produce a material that possesses cementitious properties (Chapter 2). Alkaline activated cement, alkaline activated slag and fly ash, and geopolymers are all considered to be alkaline activated cementitious systems, however, it is proposed in the thesis that the structures of these materials are vastly different, resulting from different chemical mechanistic paths as described earlier in Chapter 2.

It is commonly acknowledged that calcium silicate hydrate (CSH) is the major binding phase in Portland cement (Gani, 1997; Taylor, 1964a) and alkaline activated cement (Taylor, 1964b) as discussed in Sections 2.2 and 2.3. In contrast, the binding property of geopolymers is generally assumed to be the result of the formation of a three-dimensional amorphous alkaline aluminosilicate network (van Jaarsveld and van Deventer, 1999a, b; van Jaarsveld et al., 1997; Davidovits, 1999, 1991; Davidovits et al., 1990; Davidovits and Davidovics, 1988) as described previously in Section 2.4. This chapter will revisit some of these results, which are of more relevance to the further discussion presented here.

Davidovits (Davidovits, 1991; Davidovits and Davidovics, 1988) proposed that geopolymers are formed by polymerisation of individual aluminate and silicate
species, which are dissolved from their original sources at high pH in the presence of alkaline metals. The resultant products have the general formula $M_{n-}\cdot[-Si-O_2]_z\cdotAl-O]_n\cdotwH_2O$ where $M$ is the alkaline element, $z$ indicates the presence of a bond, $z$ is 1, 2 or 3 and $n$ is the degree of polymerisation. Theoretically, any alkaline cation can be used as the alkaline element ($M$) in the reaction, however the majority of research, so far, has focused on the effect of sodium ($Na^+$) and potassium ($K^+$) ions (Xu, 2002; Xu et al., 2001; van Jaarsveld, 2000; Xu and van Deventer, 2000; Davidovits, 1999; van Jaarsveld and van Deventer, 1999a, b; van Jaarsveld et al., 1999). It has not been clearly shown whether other alkaline and/or alkaline earth cations, including calcium will participate in the reactions in a similar way.

The major difference between geopolymers and Portland cement in terms of their chemical composition is calcium, which is not essential in any part of a basic geopolymeric structure. Given that CSH will be formed when soluble calcium and silicate species are present in a neutral to mild pH environment (Gani, 1997; Taylor, 1964a, b), it is proposed that provided sufficient calcium is added to a geopolymeric system, a CSH based cementitious material may form instead.

In recent years, some studies have been conducted on various metakaolin (MK)/lime (calcium hydroxide) and MK-blended cement systems (Alonso and Palomo, 2001a, b; Cabrera and Rojas, 2001; Frias and Cabrera, 2001; Coleman and McWhinnie, 2000; Frias et al., 2000). Cabrera and co-workers found that the activation of metakaolin in the presence of calcium hydroxide will cause rapid formation of CSH, $C_2ASH_8$ (stratlingite) and $C_4AH_{13}$ (tetracalcium aluminate hydrate) (Cabrera and Rojas, 2001; Frias and Cabrera, 2001; Frias et al., 2000).

Alonso and Palomo (2001a, b) found that under a highly alkaline environment (by the substantial addition of sodium hydroxide to the system), the alkaline activation of metakaolin in the presence of calcium hydroxide would lead to the formation of an amorphous sodium aluminosilicate, which has the same characteristics as a geopolymeric gel. The geopolymeric gel formed was found to be similar to that obtained when metakaolin was activated in the absence of calcium hydroxide. CSH gel was also formed as a secondary product when metakaolin was activated in the presence of calcium hydroxide.
The nature of the end product as a result of the alkaline activation of an aluminosilicate source in the presence of a calcium source is therefore dependent on various factors, including (Alonso and Palomo, 2001a, b; Cabrera and Rojas, 2001; Frias and Cabrera, 2001; Frias et al., 2000): the elemental composition, mineralogy, and physical properties (e.g. surface properties, particle size distribution) of both aluminosilicate and calcium sources, the alkalinity, the nature of the soluble alkaline metal present, as well as pre-treatment of materials and/or the curing conditions. Figure 4.1 shows the conceptual mapping of the likely reaction products formed when calcium is added to a geopolymeric system.

There is currently no published literature on the relationship between the geopolymer and CSH based on the MK/GGBFS system. The chemical reactions taking place in the MK/GGBFS system are expected to be more complex than in the MK/lime system, because GGBFS consists of a mixture of glassy phases reacting at different rates. Moreover, there are quite a number of impurities (e.g. iron, magnesium) present in the GGBFS that can affect the reactions taking place during alkaline activation.

The MK/GGBFS mass ratio, and the Na₂O/SiO₂ molar ratio in the alkaline activator solution were the main parameters investigated in this study. The findings from this work are fundamental to any further work on the relationship between geopolymers and Portland cement in terms of their respective chemical mechanisms as shown in the subsequent chapters of the thesis.

4.1.2 Metakaolin (MK)
MK is used as the aluminosilicate source throughout the thesis as discussed in Section 3.1. In contrast to silica fume and fly ash, MK is not an industrial by-product commonly used as a cement replacement and construction material. Metakaolin is produced by controlled calcination of kaolin at 400-750°C. MK is a highly reactive metastable clay that is essentially an anhydrous aluminosilicate (Newman, 1987).

Chapter 2 has introduced the substantial amount of research that has been conducted on the synthesis of metakaolin from kaolin, the alkaline activation of metakaolin and
the pozzolanic reaction involving metakaolin in cementitious systems. Metakaolin was chosen as the primary aluminosilicate source in this study because it is widely used as an aluminosilicate source in geopolymeric systems (van Jaarsveld et al., 2002; Phair and van Deventer, 2001; Davidovits, 1999; Krivenko et al., 1999; Palomo et al., 1999; Silva et al., 1999; Palomo and Glasser, 1992) as well as in the formation of zeolites (Akolekar et al., 1997; Atkins et al., 1995; Murat et al., 1992; Madani et al., 1990). Moreover, it has been widely used as a mineral admixture in Portland cement (Asbridge et al., 2002, 2001; Qian and Li, 2001; Roy et al., 2001; Coleman and McWhinnie, 2000; Krivenko et al., 1999; Coleman and Page, 1997; Atkins et al., 1995; Oriol and Pera, 1995; Salvador, 1995; Ambroise et al., 1985; Murat, 1983a, b; Murat and Cornet, 1983).

The synthesis of metakaolin from kaolin involves the calcination of kaolin to approximately 400-750°C for an average of 2-24h (Shvarzman et al., 2003; Granizo et al., 2000; Huertas et al., 1999; Murat et al., 1992; Newman, 1987). Kaolin is a dioctahedral 1:1 layer silicate mineral with formula Si$_2$O$_5$(OH)$_4$Al$_2$. As shown in Equation 4.1, the dehydration by thermal treatment, converts kaolin to metakaolin, which is much more reactive than the starting material, due to its glassy semi-crystalline to amorphous structure as determined by powder x-ray diffraction (Akolekar et al., 1997).

\[
\begin{align*}
700^\circ C \\
\text{Si}_2\text{O}_5\text{(OH)}_4\text{Al}_2 \text{ (kaolin)} & \longrightarrow \text{Al}_2\text{Si}_2\text{O}_7 \text{ (metakaolin)} + 2\text{H}_2\text{O} \\
& \text{(4.1)}
\end{align*}
\]

According to Mandani et al. (1990), the calcination step involves the dehydroxylation and the formation of the quasi-stable dehydroxylated phases. It was found by Mandani et al. (1990) that the dehydroxylation of the kaolin was completed at 750°C, the partial breaking of the tetrahedral sheet takes place at 850°C, and the segregation of amorphous silica occurs at 980°C. Metakaolin is believed to be a defect phase in which tetrahedral silica layers of the original clay structure are largely retained; adjacent are the AlO$_4$ tetrahedral units derived from the original octahedral layer of the kaolin (Akolekar et al., 1997; Madani et al., 1990; Newman, 1987).
4.1.3 Ground Granulated Blast Furnace Slag (GGBFS)

The American Society of Testing and Materials (ASTM) defines blast furnace slag as the "the non-metallic product consisting essentially of calcium silicates and other bases that is developed in a molten condition simultaneously with iron in a blast furnace." Blast furnace slag is therefore produced as a by-product during the manufacture of iron and steel. If not utilised, slag is a waste, which goes to landfill. Over three million tonnes of slag per year is produced in Australia (National Occupational Heath & Safety Commission, 2002), all of which could potentially be recycled as a valuable raw material, principally for the construction industry. In Australia, granulated blast furnace slag is used as a cementitious material and air-cooled blast furnace slag is used as an aggregate (QCL Group, 1999).

In the production of iron, the blast furnace is charged with iron ore, fluxing agents (usually limestone and/or dolomite), and coke as both fuel and reducing agent. Oxygen in the preheated air that is blown into the furnace combines with the carbon of coke to produce the needed heat and carbon monoxide. At the same time, the iron ore is reduced to iron, mainly through the reaction of carbon monoxide with the iron oxide to yield carbon dioxide (CO₂) and metallic iron. The fluxing agents dissociate into oxides and CO₂. The oxides combine with silica and alumina to form slag. The physical characteristics such as density, porosity, and particle size, are affected by the cooling rates of the slag and its chemical composition. Three different types of blast-furnace slag are commonly produced based on the cooling methods: air-cooled, expanded and granulated (Kalyoncu, 2001). In general, slag of all types must be allowed to 'cure' or age for a period of time, before it can be used in various applications (e.g. as a cementitious material) (Kalyoncu, 2001).

Granulated slag is produced by quenching the molten slag into glass granules with the use of high-pressure water jets (Kalyoncu, 2001). The blast furnace slag is almost instantaneously brought to a temperature below the boiling point of water forming fine sand-sized particles of material high in glass. The granulated slag is then de-watered and stored or dried and ground (QCL Group, 1999). Quenching prevents the crystallisation of minerals constituting the slag composition, thus resulting in a granular, glassy aggregate (Kalyoncu, 2001). This slag is crushed, pulverised, and
screened for use in various applications, particularly in the cement industry, owing to its pozzolanic characteristics as discussed in Chapter 2.

Granulated blast furnace slag (GBFS) is predominately ground to Portland cement fineness and is used as a replacement for Portland cement in concrete mixes or is blended with Portland cement at the batching facility. Ground granulated blast furnace slag (GBFS) is valued for its concrete enhancing properties and is becoming widely used in high-performance concrete applications. Availability of GGBFS is dependent on iron and steel production level and time of the construction cycle. GGBFS is used in the thesis as the primary calcium source.

4.2 Experimental Procedures

Refer to Section 3.2 for a detailed description of the geopolymer sample synthesis. A description of all analytical techniques used in this chapter can be found in Section 3.4. The following section will therefore only highlight the information most relevant to the current chapter.

4.2.1 Materials

MK used in the synthesis was obtained from ECC International under the brand name of MetaStar 402. This commercial metakaolin was purified before calcination, and it had less than 0.1 wt.% of CaO, and an over 95% of combined wt.% of silica (SiO₂) and alumina (Al₂O₃) as shown in Table 4.1. The oxide composition was obtained by X-Ray Fluorescence (XRF) analysis, using a Siemens SRS 3000 instrument as described in Section 3.3.1. Based on the specification supplied by the manufacturer, the particle size distribution of MK is 100% <10μm. Further analysis using Coulter LS130 optical particle size analyser (Section 3.4.6) found that the average particle size of MK is 1.895μm as shown in Table 4.2.

Figure 4.2 presents the diffractogram obtained of MK using a Phillips PW1800 diffractometer using a CuKα anticathode (Section 3.4.2) at a scanning rate of 2°/minute from 5 to 70° 2-theta. MK consists mainly of glassy phases with low-intensity peaks corresponding to muscovite (potassium aluminium silicate hydroxide
with JCPDS 07-0042) as compared to the diffraction patterns of the Joint Committee on Powder Diffraction Standards (JCPDS) data.

Figure 4.3 shows a SEM image of raw MK (Section 3.4.4). The micrograph highlights the glassy structure of the raw MK used. Figures 4.4 and 4.5 show TEM micrographs of MK obtained (Section 3.4.5). Figure 4.4 highlights the hexagonal structure of MK, while Figure 4.5 shows the small percentage of the fibrillar structure (marked “A” on the micrograph) present in the raw material. The hexagonal structure is the prominent feature of MK, even though the hexagonal shape is slightly distorted, it still retains the hexagonal shape of kaolin (the natural mineral, prior to calcination), as shown in Figure 4.6. This is in agreement with previous studies that metakaolin is a defect phase in which tetrahedral silicon layers of the original clay structure are largely retained (Akolekar et al., 1997; Madani et al., 1990; Newman, 1987). Unless otherwise stated, all SEM and TEM micrographs presented in this chapter were captured by a Philips XL30 scanning electron microscope and a Philips EM420 transmission electron microscope respectively.

It is assumed in this study that all calcium present in the system originates from ground granulated blast furnace slag (GGBFS). Table 4.1 shows the oxide composition of GGBFS. It contains 43% CaO, 34.4% SiO₂, 14.1% Al₂O₃ and 6.3% MgO. GGBFS was obtained from Independent Cement with an average particle size of 21.54μm as shown in Table 4.2. GGBFS consists mainly of glassy phases with a detectable amount of gypsum (calcium sulphate dihydrate with JCPDS 33-0311) as shown in Figure 4.2. Figure 4.7 shows a SEM image of GGBFS, which shows the heterogeneous nature of the material.

The sodium silicate solution used in the experiments described in this Chapter was supplied by PQ Australia under the brand name of Vitrosol N48 (28.7 wt.% SiO₂, 8.9 wt.% Na₂O and 62.4 wt.% H₂O; density 1370kg/m³). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout. Fine washed sand (100% <2mm) was used as the aggregate in samples that were subjected to compressive strength testing. Samples subjected to other analyses were prepared without the addition of washed sand.
4.2.2 Synthesis

A full detailed description of how binders were synthesised in the thesis is presented in Section 3.2. Presented here is a description of sample preparation specific to this Chapter. Alkaline activator solutions with two different molar ratios between SiO$_2$ and Na$_2$O (Modulus = Ms = SiO$_2$/Na$_2$O = 2.0 and 1.2) are used, and six mass ratios between MK and GGBFS (MK/(MK+GGBFS) = 0, 0.2, 0.4, 0.6, 0.8 and 1) are used in this study. The mass ratios between the alkaline mix (sodium hydroxide and sodium silicate solution) and dry mix (MK and GGBFS) are 1.45 and 1.63 for Ms = 2.0 (Matrices M1 to M6) and 1.2 (Matrices N1 to N6) respectively. As suggested in Section 3.2, these particular ratios were chosen to provide for equal moles of water present in the structures of all the matrices synthesised. For samples subjected to compressive strength testing, washed sand (with mass ratio = sand/(MK + GGBFS) = 3) was added to the geopolymeric paste before pouring into the moulds. Samples were examined using various techniques at specific time intervals (up to 720 days) following synthesis. Table 4.3 presents a summary of all the matrices synthesised in this study.

4.2.3 Analysis

Compressive strength testing was performed as per Australian Standard (AS1012.9-1999) using three 50mm diameter cylinders with a 1:2 diameter to length ratio. All compressive strength measurements were taken as the average of strength results of three samples. An ELE International Auto Compressive Machine was used. Before testing, the top face of the specimen was cut in parallel with the bottom face by using a diamond saw. The top surface of the sample was capped with fast setting Boral Dental Plaster to ensure the diameter and length ratio remained at 1:2 as described in Section 3.4.7. The sample was left overnight at room temperature and atmospheric pressure. The compressive test was conducted on the following day.
4.3 Results and Discussion

The effects of the MK/(MK+GGBFS) mass ratio and the SiO₂/Na₂O molar ratio on the compressive strength of MK-GGBFS binders are presented in Sections 4.3.1 and 4.3.2 respectively. This is followed by a discussion on the structure of the resultant geopolymer product using XRD (Section 4.3.3) and microanalysis (Sections 4.3.4 and 4.3.5). A detailed discussion on the coexistence of CSH and geopolymeric phases in the system will be presented in Section 4.3.6.

4.3.1 Effect of the MK/(MK+GGBFS) Ratio on Compressive Strength

The effects of different MK/(MK+GGBFS) mass ratios and alkalinity on the mechanical strength of the resultant products are summarised in Table 4.4 (Ms = 2.0) and Table 4.5 (Ms = 1.2), and Figure 4.8 and Figure 4.9. The most significant factor that affects the compressive strength is the ratio between MK and GGBFS. These results demonstrate that an optimum MK/GGBFS ratio exists, which provides the highest compressive strength of the resultant matrix for a given alkaline concentration.

In a low alkaline system (Ms = 2.0), the resultant compressive strength of the matrices increased when a moderate amount (20 wt.% of the total mass between MK and GGBFS) of GGBFS was added to the system (Matrix M2). The compressive strength of Matrix M2 after 720 days is 65.4MPa as opposed to 35.2MPa and 9.8MPa for Matrices M1 (with 100% of MK) and M6 (with 100% GGBFS) respectively. The difference between the compressive strength values of Matrices M1 and M2 (with 20 wt.% of GGBFS) was found to increase from 7.2MPa after 1 day to 30.2MPa after 720 days.

The compressive strength of matrices containing only MK (Matrices M1 and N1) was found to increase with time, however this gain (from 1 day to 720 days) was only 3.1MPa and 4.5MPa for Matrices M1 and N1 respectively. This improvement in compressive strength for these MK-binders was small, in comparison to greater than 26MPa increase recorded for Matrix M2 over the same time period. The compressive strength development of the matrices containing only MK (Matrices M1 and N1) was therefore limited after 1 day. These results indicate that the moderate addition of
GGBFS to a metakaolin-based geopolymeric system will improve the mechanical property and enhance the durability of the resultant matrix over time.

The excessive addition (> 40wt.%) of GGBFS (Matrices M5 and M6) was, however, found to be destructive as shown in Table 4.4. The resultant compressive strength of these matrices was found to be significantly less than the other matrices containing more MK. The difference in compressive strength between Matrices M2 (20% of GGBFS) and M5 (80% of GGBFS) increases from 19.3MPa after 1 day to 52.7MPa after 720 days. Matrices M5 and M6 rapidly lost their mechanical property after 7 days following synthesis. The compressive strength recorded by these matrices (< 5MPa) was below the lowest detectable limit for the ELE International Auto Compressive Machine after 90 days, and then it slowly reached 12MPa and 10MPa after 720 days respectively. By physical observation of these matrices containing a substantial amount of GGBFS, it was found that cracks had developed. When external force was applied, therefore the whole sample crumbled. The durability of matrices containing a substantial amount (> 40% wt) of GGBFS is poor.

For an alkaline activator solution of high alkalinity (Ms = 1.2) (Table 4.5), it was also found that the addition of a moderate amount of GGBFS (Matrix N2) gave an optimum compressive strength result. Increasing the amount of GGBFS added (> 20wt.%), resulted in binders with poor strength. Matrices N5 (80% GGBFS) and N6 (100% GGBFS) become particularly weak with time, whereby the compressive strength of these matrices decreased rapidly until the matrices deteriorated and crumbled after approximately 240 days.

In order to explain these results, it is important to note that MK has a considerably smaller particle size than GGBFS (1.895µm compared to 21.54µm) as shown in Table 4.2. When dissolution takes place therefore, it is anticipated that MK will be more reactive than GGBFS due its smaller particle size. Subsequently, the viscosity of the initial suspension with more MK will be higher than the one with more GGBFS. In the thesis, the water content in the all samples was kept constant. Since the same amount of water was used in all binders, the gel resulting from the activation of GGBFS was thinner than the one resulting from the activation of MK. It is therefore believed that if excess water in the thinner gel is not consumed during the hydration
process, free water will diffuse out of the matrices with time. Due to the considerable molecular size of water, the diffusion of water out of the matrices may leave behind more inner pores within the structure, which may consequently induce cracking throughout the matrices. The loss, by evaporation, of significant amount of water should also induce shrinkage. This is evidenced by the observed development of cracks, and poor compressive strength values in matrices containing mainly GGBFS (Matrices M5, M6, N5 and N6).

4.3.2 Effect of Alkalinity (SiO$_2$/Na$_2$O Molar Ratio) on Compressive Strength

In order to study how alkalinity affects the reaction path for dissolved calcium in geopolymerisation, samples were synthesised with alkaline activators of two different concentrations of sodium hydroxide (Ms = 1.2 and 2.0).

For the geopolymeric binder with 100% metakaolin (Matrices M1 and N1), it was found that the compressive strength of these matrices increased with increasing sodium hydroxide concentration. This observation is in agreement with previous work, which showed that geopolymerisation is enhanced in a highly concentrated alkaline environment (Phair et al., 2000; van Jaarsveld, 2000). It is generally believed that the initial dissolution process is caused by the presence of hydroxyl ions as described earlier in Chapter 2. The presence of a high concentration of hydroxyl ions will therefore favour the dissolution of silicate and aluminate species, subsequently promoting further polymerisation.

The difference in compressive strength between Matrices M1 and N1 is comparatively small to the change between matrices synthesised at different alkalinitities with the addition of GGBFS. The difference between the compressive strength of Matrices M1 and N1 was only 3MPa and 5MPa after 1 and 720 days respectively. The difference between Matrices M2 and N2 increased from 6.5MPa after 1 day to 20.9MPa after 720 days, in favour of Matrix M2. In contrast to the results obtained for Matrices M1 and N1, the compressive strength of MK-GGBFS binder increases with decreasing amount of sodium hydroxide used. This indicates GGBFS plays a significant role in controlling the compressive strength of the MK/GGBFS system, and it is dependent on the alkalinity of the alkaline activator used.

80
Despite the improved compressive strength achieved consistently by Matrix N2 in comparison to Matrix N1 upon the small addition of GGBFS, this difference (~3MPa) is comparatively small in a highly alkaline environment \( (Ms = 1.2) \). In contrast, the difference in compressive strength between matrices with a moderate addition of GGBFS (Matrix M2) and without GGBFS (Matrix M1) synthesised under a low alkalinity increases from about 7MPa (1 day) to over 30MPa (720 days) as discussed earlier. This result suggests that the geopolymeric gel is the component that contributes to the resultant strength of the binder under high alkalinity and the small percentage of calcium species will have little effect on the compressive strength. In contrast, under low alkalinity \( (Ms = 2.0) \), the presence of the alkaline activated product of GGBFS has a positive impact on the binding property, thus the compressive strength.

Strength development of Portland cement involves the formation of CSH and calcium hydroxide, and it is generally believed that the CSH gel is the component that gives the strength to the resultant binder (Taylor, 1964a). The main role of GGBFS is assumed to contribute dissolved calcium species, which will react with silicate and aluminate to form various forms of calcium silicate hydrates and calcium aluminium hydrates in the MK-GGBFS system. However, the pH value in both systems investigated in the current system is approximately 14. Phair et al. (2000) have shown that the solubility of calcium decreases with increasing pH, which is attributed to the formation of calcium hydroxide. Furthermore, with the high concentration of NaOH being used in the current system, it is well documented that the solubility of Ca will be depressed as a consequence of the common ion (OH\(^{-}\)) effect, and that the solubility of Ca(OH)\(_2\) is much lower than that of the alkaline hydroxide in a cementitious system (Sagüés et al., 1997). Moreover, it is also discussed that the possible formation of CSH decreases with increasing pH. Martinez-Ramirez and Palomo (200a, b) found that CSH decomposes under highly alkaline conditions by forming quartz and Ca(OH)\(_2\). Based on these findings, and with the excessive amount of sodium hydroxide being used in the current system, it is anticipated that precipitation of calcium hydroxide will take place when the MK and GGBFS are mixed in such a highly alkaline medium. Calcium hydroxide is highly unstable, which will further react with carbon dioxide in the air to from calcium carbonate.
(carbonation) (Glukhovsky, 1994). It is generally agreed that the presence of excess calcium hydroxide in the resultant structure and the subsequent carbonation process are the main cause of the deterioration of concrete (Glukhovsky, 1994).

In addition, the precipitation of calcium hydroxide will also prevent calcium species forming CSH, C2ASH8 (stratlingite) and C4AH13, which are commonly found as major products in the activation of MK in the presence of calcium hydroxide (Frias and Cabrera, 2001). Thus, in systems where there is excess GGBFS present, it is expected that a substantial amount of calcium hydroxide will be formed. Subsequently, the mechanical properties of the resultant binder will be weakened, which leads to a rapid reduction in strength with time.

Previous studies (Lee and van Deventer, 2001; Phair and van Deventer, 2001; van Jaarsveld, 2000) have found that calcium has a positive impact on the resultant compressive strength of geopolymeric binders. The current findings are in agreement with these studies. It is confirmed that the addition of a moderate amount of calcium (from an amorphous calcium silicate source) in the current MK-GGBFS system will improve the mechanical properties of the matrices. However, it is yet to explain why the presence of calcium will play such a significant role in determining the properties of the resultant binder, especially in the low alkaline environment (Ms = 2.0). Many attempts have been made to explain the increase in compressive strength in geopolymeric binders synthesised in the presence of a calcium source, however, the investigation is still incomplete. Before any progress can be made towards understanding the chemical mechanism involved in the alkaline activation of MK in the presence of GGBFS, it is essential to examine and analyse the products at different hydration stages.

4.3.3 Crystallinity of Hydration Products

XRD was used to study the changes in crystallinity before and after alkaline activation. It should be noted that the reactants used and most of the binders produced in this study contain a very high percentage of amorphous to semi-crystalline phases. It is therefore difficult to identify all the crystalline phases according to JCPDS.
The x-ray diffractograms (Figures 4.10 and 4.11) show the effect of different MK/(MK+GGBFS) mass ratios and Na₂O/SiO₂ molar ratios on the crystallinity of the geopolymeric material at 28 days. It can be seen from Figures 4.10 and 4.11 that there is a “hump” starting from 20° 2-theta to approximately 40° 2-theta for most of the matrices. Figure 4.12 enlarges the region between 20° to 40° 2-theta, in which the “hump” is located along with various other major diffraction peaks. The XRD diffractograms presented in Figures 4.13 and 4.14 are plotted as the difference between the diffractograms of the resultant binder at 28 days before and after the alkaline activation, which was calculated by subtracting “diffractogram before activation” from “diffractogram after activation”. The use of “difference” diffractogram will highlight the phases created and destroyed during the alkaline activation.

As shown earlier in Figure 4.2, both MK and GGBFS consist mainly of amorphous phases with low-intensity peaks corresponding to muscovite and gypsum respectively. These minor crystalline phases were totally or partially dissolved when the materials were alkaline activated (as observed from Figures 4.10 to 4.14). These diffractograms show that despite the alkaline activation, the resultant product remains amorphous to semi-crystalline, with the formation of a small percentage of crystalline or semi-crystalline phase associated with diffraction peaks at various d-spacings as highlighted. It is difficult to distinguish and identify the various phases present (according to the JCPDS standard), due to the low intensity and the possible overlapping of various peaks.

It is shown in Figure 4.15 that there is no new crystalline phase formed as a result of the alkaline activation of MK in the presence of GGBFS. In fact, the crystallinity of the resultant product remains highly amorphous even after an extended period of time. The XRD diffractograms of Matrix M2 at different time periods (Figure 4.15) indicate that the mineralogical composition of the geopolymeric product remains relatively constant from early stage (7 days) to almost 2 years after synthesis.

As discussed earlier, there is a hump starting at about 20° through to 40° 2-theta in the XRD diffractograms of MK binders (Matrices M1 and N1) synthesised using different
Na₂O/SiO₂ ratios. Previous XRD studies (Phair et al., 2000) on geopolymeric binders have reported similar characteristics. It was suggested that the hump is due to the presence of amorphous silica in the binder (Phair et al., 2000; van Jaarsveld and van Deventer, 1999a; van Jaarsveld et al., 1999). When comparing the binders before and after the alkaline activation for the MK-binder (Figure 4.13, Matrix M1; Figure 4.14, Matrix N1), it was found that there are only limited changes to the intensity of the hump at around 28-32° 2-theta for both 100% MK binders activated regardless of the Na₂O/SiO₂ ratios used. Since the XRD humps found at 28 to 32° 2-theta have similar characteristics, it can be concluded that the crystallinity of the resultant product from the alkaline activation of MK is independent of Na₂O/SiO₂ ratio used within the range studied in this investigation.

There is no new crystalline peak associated with the alkaline activation of GGBFS as shown in Figures 4.10 to 4.15. Therefore it can be concluded that crystalline CSH is not a product, or it is not a dominant product formed as a result of the alkaline activation of GGBFS under the conditions studied. This is in agreement with previous findings by van Jaarsveld and van Deventer (1999a) that crystalline CSH is not formed under high pH (pH >14) environment. However, it may be possible to form amorphous CSH within a geopolymeric gel in the resultant product. This will be examined in Section 4.3.3.

It is not possible to identify the small percentage of crystalline or semi-crystalline product associated with the various XRD diffraction peaks at various locations (e.g. at ~23.5, 26.5°, 29.5° and 31.5° 2-theta) formed within the geopolymeric product. The range of possible products that could be associated with these characteristics peaks is too wide and the intensities of these peaks are too low, to draw a reasonable conclusion to identify these difference phases at this stage.

It should also be noted that the characteristic peaks associated with crystalline calcium hydroxide (portlandite with JCPDS 4-0733) were not observed in the resultant structure. However, this does not exclude the possible formation of amorphous calcium hydroxide. As discussed earlier, it is expected that calcium hydroxide will precipitate from the alkaline solution once soluble calcium species are present in the solution phase during the initial dissolution step.
4.3.4 Microstructure of MK Binders

Electron microscopy was employed in the current work to examine the microscopic effect of GGBFS on the alkaline activation of MK. Regardless of the Na₂O/SiO₂ ratio used, when metakaolin is activated by an alkaline solution, a geopolymeric binder will be the dominant product formed, with no other phases of substantial quantity being detected by XRD analysis as shown in Section 4.3.3. Figure 4.16 shows a representative SEM image of the microstructure of a geopolymeric product (Matrix M1) with 100% MK alkaline activated using Ms = 2.0. The average Al₂O₃/SiO₂ molar ratio of this geopolymeric product was found to be ~ 0.26.

Figure 4.17 shows a representative TEM image of a geopolymeric binder (Matrix M1), which was found to consist of the following four different micro-phases:

(A) Undissolved metakaolin particle, which retained the original hexagonal shape as identified in Figure 4.4. The elemental composition of this phase was found to be similar to the original hexagonal MK plate under the TEM examination;

(B) Undissolved fibrillar metakaolin particle similar to those identified in Figure 4.5, having a similar morphology and elemental composition;

(C) Some weakly crystalline sodium aluminosilicate particles, which are proposed to be a constituent of the geopolymeric product. These particles were identified through an elemental analysis conducted randomly across the specimen. They were found to be crystalline to semi-crystalline through the electron diffraction patterns presented in Figure 4.18. The particles were commonly found as circular plates with an average diameter of ~ 0.2μm to ~ 0.5μm, which have a similar Al₂O₃/SiO₂ molar ratio as raw MK hexagonal plate and particle “A” as identified in Figure 4.17, but with a much higher sodium content. These particles are proposed to be the result of the alkaline activation of the surface of MK, and that the original hexagonal plate is believed to transform into its circular shape as the result of alkaline
activation, before being fully dissociated into different silicate and aluminate species; and

(D) Amorphous aluminosilicate, which is believed to be the other constituent of the geopolymeric product. This phase was found to have no regular shape or morphology under TEM. It is characterised with a 2-ring electron diffraction pattern that is highly diffused (slightly distorted and poorly defined) as shown in Figure 4.19. This kind of structure is often resembled by a short-range order where any order present in the structure involves less than 20 atoms in length (van Jaarsveld, 2000). The elemental composition of this amorphous aluminosilicate phase was found to vary substantially across the phase, in which the average molar ratio between Al$_2$O$_3$ and SiO$_2$ varied from $\sim 0.11$ to 0.37.

Comparing Figure 4.17 to the TEM image of raw MK as shown in Figures 4.4 and 4.5, it can seen that most of the hexagonal particles of raw MK have reacted and thus, disappeared as the result of alkaline activation. The geometric shape of the alkaline activated product of MK was therefore found to be more “rounder” (Figure 4.17 particle “C”), as discussed earlier. Hence, the alkaline activation of MK is suggested to be a surface reaction, with silicate and aluminate species dissociated from the surface of metakaolin. This is the possible reason why particle “C” in Figure 4.17 is observed in the resultant product, and that the average diameter of these particles is smaller than the particle size of the hexagonal plate in MK. The silicate and aluminate species dissociated from MK will undergo polymerisation to form higher ordered oligomers and thus the geopolymeric gel (amorphous sodium aluminosilicate network). This geopolymeric gel is identified as particle “D” in Figure 4.17. The current TEM result and observations are in agreement with the chemical mechanism proposed by Xu and van Deventer (2000). Subsequently, the different degree of polymerisation that has taken place in the system may also explain why there exists a large variation of the Al$_2$O$_3$ to SiO$_2$ molar ratio for particle “D” throughout the resultant product. This observation also highlights the fact that geopolymerisation is an on-going process.
4.3.5 *Microstructure of MK-GGBFS Binders*

Figure 4.20 shows a representative scanning electron micrograph of a resultant binder (Matrix M2) containing 80 wt.% of metakaolin and 20 wt.% of GGBFS with $M_s = 2.0$ at 14 days. Two separate phases (Areas A and B) were formed as a result of the alkaline activation of metakaolin in the presence of GGBFS. The formation of two separate phases within a single binder can be clearly observed from the vast difference between the optical contrast of the two regions, in which it is commonly acknowledged that the intensity of reflected electrons is proportional to the atomic number in the object. The brighter region (Area B) is anticipated to contain atoms with atomic number much higher than that of the darker region (Area A).

Moreover, elemental analysis was conducted on the sample and the results are summarised in Table 4.6. It was found that the elemental composition of Area A was dominated by silicon, aluminium and sodium with less than 2 wt.% of calcium, while the elemental composition of area B was dominated by silicon and calcium with some sodium and less than 3 wt.% of aluminium. It is therefore confirmed that Areas A and B are different in composition. The brighter contrast observed in Area B is the result of the high concentration of atoms with higher atomic number (i.e. calcium) present in the region.

The concentration of each element was found to be consistent within Areas A and B and there is a narrow interfacial area between the two regions. Area A is proposed to be a geopolymeric binder, which has similar characteristics to the geopolymeric binder formed in the absence of GGBFS. This result is in agreement with previous observations by Alonso and Palomo (2001a, b), whereby the geopolymer formed as the result of the alkaline activation of MK in the presence of Ca(OH)$_2$ has the same characteristics as that formed in the absence of Ca(OH)$_2$. Traces of calcium within this geopolymeric phase (Area A) originated from and diffused outward from the GGBFS.

Likewise, the elemental composition of Area B is consistent within the region. Calcium and silicon are the main elements in this area, in which aluminium and sodium are of much lower concentrations. Therefore it is suggested that the phase present in Area B could be some form of CSH (calcium silicate hydrate). However
this CSH is different from the one generally formed from the hydration of Portland cement or amorphous calcium silicate in raw slag with a much lower CaO/SiO₂ ratio than that in Phase B. The concentration of aluminium in this phase is low when it is considered that both MK and GGBFS contain a relatively high level of aluminium (Table 4.1). Therefore it is thought that some of the aluminium originating from the GGBFS would diffuse outward from the surface of GGBFS and participate in the geopolymerisation. In fact, the coexistence of the separate geopolymeric gel and CSH gel within a single binder remains the dominant feature of the alkaline activated MK-GGBFS system even after an extended period (> 2 years old) (Figure 4.21). Further discussion on the microanalysis of the CSH and geopolymeric gels coexisting in the same binder will be further discussed in Chapter 5.

Figure 4.22 shows a representative transmission electron micrograph of Matrix M3 resulting from the alkaline activation of 60% metakaolin and 40% GGBFS. Through the examination of Matrices M1 and M3 under the TEM (Figures 4.17 and 4.22), the most notable difference observed between the two was the absence of undissolved metakaolin particles (particles “A” and “B” as identified in Figure 4.17). Most of the metakaolin particles in Matrix M3 were dissolved or the concentration of undissolved MK has become too low to make it possible to be detected under TEM. The rate of dissolution is postulated to be dependent on the alkaline concentration used in activating both MK and GGBFS, and the compressive strength of resultant binder is postulated to be dependent on the extent of the dissolution of both starting materials. This postulate will be later confirmed and discussed, when thorough dissolution tests were conducted on the starting materials in subsequent chapters.

According to the XRD analysis as described earlier in Section 4.3.3, there is no detectable amount of new phase forming as the result of the alkaline activation of MK in the presence of GGBFS. However, based on the electron diffraction analysis conducted randomly over specimens with different amount of GGBFS added as shown in Figure 4.23, some undefined crystalline phases do form as the result of alkaline activation. These crystalline phases were found to increase with increasing GGBFS being added to the system. However, it should be noted that despite the increase in quantity of these crystalline phases in the resultant matrix, they remain to
be the minor constituents. Due to the low concentration of these phases, these crystalline phases cannot be readily detected by XRD.

Figure 4.23 shows the electron diffraction pattern of a crystalline phase present in Matrix M3, while Figure 4.24 shows a well-defined electron diffraction ring pattern of a semi-crystalline phase present commonly found in a geopolymeric binder with a substantial amount of GGBFS added. In comparison to Figure 4.19, the ring pattern in Figure 4.24 still contains only 2 rings, but they are much sharper. Moreover, some individual electron dots making up the electron ring can be clearly observed in Figure 4.24, which indicates that the individual crystals are getting bigger along with the bigger grain size in the resultant product containing an increasing amount of GGBFS. These all indicate that the resultant product in a binder containing more GGBFS is more crystalline.

Even though it is possible to observe and distinguish these crystalline phases forming in the MK-GGBFS system, it is still not possible to identify and characterise them in detail. A low concentration, and a large degree of variation within the microstructure of these phases, as well as a small specimen size used in the examination have made the identification process difficult by giving inconsistent results. However, it is suggested that these phases contain a range of products, but mainly crystalline calcium hydroxide and crystalline calcium silicate hydrate.

For the same alkalinity, but when more GGBFS was added to the system, the coexistence of geopolymeric gel and CSH gel was still the prominent feature as observed through the SEM examination (Figure 4.25). However, the coexistence of the two separate phases disappears or the geopolymeric gel has become too small to be observed when more than 80 wt.% of GGBFS was added (Matrix M4). The major products formed under such conditions are various types of calcium silicate hydrate, calcium silicate aluminate and calcium aluminosilicate hydrate. However, due to the highly amorphous nature of the resultant products, it is not possible to determine whether phases such as $\text{C}_2\text{ASH}_8$ and $\text{C}_4\text{AH}_{13}$ were formed.

When the concentration of NaOH in the alkaline activation increased ($M_s = 1.2$), a clear coexistence of geopolymeric gel and CSH gel could not be observed unless a
substantial amount of GGBFS (>50 wt.%) was used initially as shown in Figure 4.26. The morphology of the major product formed with <50 wt.% GGBFS under high alkalinity resembles geopolymeric gel, which is similar to the one obtained under low alkalinity. The microscopic analysis on such system has also indicated that small calcium precipitates (<10μm) are scattered around the geopolymeric phase as shown in Figure 4.27. The absence of the formation of two separate phases in a highly alkaline condition has indicated that the coexistence is dependent on the alkalinity used as well as the ratio between GGBFS and MK. In fact, as the concentration of GGBFS added increases, the clear phase separation between CSH gel and geopolymeric gel is no longer the prominent feature, even in the lowly alkaline condition. Instead, increasing amount of crystalline or semi-crystalline calcium product can be observed in the binder, similar to Figure 4.28. This has indeed confirmed the observation from the TEM earlier, that the crystalline calcium phases were found to increase with increasing GGBFS being added to the system. Based on the elemental analysis, calcium silicate hydrate was clearly part of the resultant product in such system, but with a much higher average CaO/SiO₂ ratio than the one recorded for the CSH gel found coexisting in the geopolymers as discussed earlier in the current chapter.

Similar observations were found by Alonso and Palomo (2001b) when they studied the alkaline activation of MK in the presence of calcium hydroxide using thermal analysis. They found that when MK and calcium hydroxide were alkaline activated by sodium hydroxide, CSH gel was found to be the main product. However, amorphous alkaline aluminosilicate (geopolymer) was the dominant product with CSH gel being the secondary phase when the concentration of NaOH increased from 5M to 10M. The system currently investigated is more complex with amorphous calcium silicate mineral (GGBFS) being used as the calcium source and soluble silicate source being added. However the results have reconfirmed the fact that given the right condition, the formation of CSH gel and geopolymers can take place simultaneously. The nature and the amount of end products depend on many factors, of which the ratio between aluminosilicate and calcium sources and the alkalinity of alkaline activators are the dominant ones. These factors will therefore be investigated further in the subsequent chapters of the thesis.
It is proposed that calcium dissociated from the surface of GGBFS will precipitate from the alkaline medium as Ca(OH)$_2$. Dissolved calcium that does not precipitate as Ca(OH)$_2$ will participate in the formation of CSH gel in preference to the formation of calcium based geopolymers. Since there is a significant difference between the calcium concentration in the geopolymeric gel and CSH gel, it is thought that a small amount of calcium from GGBFS will diffuse outwards into the geopolymeric gel, which may explain why traces of calcium could be detected in the rich aluminosilicate phase. However, it is still unclear how the calcium is structurally bound within the aluminosilicate phase. Moreover, it is suggested that the silicate species will preferentially react with dissolved calcium rather than polymerise with soluble aluminate. Subsequently, excess aluminate species will have to diffuse outward from the calcium rich area into the geopolymeric gel as observed in this study.

From both SEM and TEM analysis, it has been shown in the current chapter that dissolved calcium from GGBFS would not participate in geopolymerisation. These results confirm what has been observed from XRD analysis (Section 4.3.3), which showed that both metakaolin and GGBFS are independently activated by alkali and that there was no calcium migration from GGBFS to metakaolin to form a geopolymeric binder. The calcium species therefore do not play a significant, if any, charge-balancing role similar to that of sodium or potassium in a geopolymer system. These results demonstrate that it would require more than simply adding a calcium source to an aluminosilicate source to form a calcium-based geopolymer. It is proposed that soluble calcium, either from the dissolution of a chemical reagent or a mineral (e.g. GGBFS), would participate in the formation of calcium silicate hydrate rather than participating in the formation of a geopolymer in a low temperature alkaline activated system. Further discussion on the chemical mechanism in the MK-GGBFS system will be presented in Chapter 5.

4.3.6 Effect of Coexistence of Geopolymeric Gel and Calcium Silicate Hydrate on Compressive Strength of Resultant Binders

The increased compressive strength of the binder with the addition of moderate amounts of GGBFS as noted in Matrix M2, can be attributed to the formation of two separate phases in a mildly alkaline condition. The results found in the current chapter have shown that given the right condition, it is possible to have both
amorphous alkaline aluminosilicate and CSH gel forming simultaneously within the same system. It is anticipated that voids and pores within the geopolymeric binder become filled with the CSH gel, which helps bridging the gaps between the different hydrated phases and unreacted particles. The formation of CSH gel within a geopolymeric binder could work as a micro-aggregate. Thus the compressive strength of the binders will increase (Tables 4.4 to 4.5 and Figures 4.8 to 4.9). However, as the calcium concentration increases, the formation of geopolymeric gel and CSH gel could compete against each other. Instead of having one phase acting as a micro-aggregate in filling up voids and holes of the resultant binder, the two reactions are competing for soluble silicates and available space for growth. Consequently, the resultant binder will be disordered with two phases of similar size, and more residual holes are produced resulting in strength reduction. The microanalysis of the CSH gel and geopolymeric gel coexisted in the same system will be examined in detail in Chapter 5. Further discussion on the chemical mechanism describing the coexistence of these two phases in enhancing the durability of the resultant product will be presented in the subsequent chapters of the thesis.

4.4 Conclusion
It was found that the geopolymeric binder formed in the presence of GGBFS is similar to the geopolymeric binder found in the absence of GGBFS. When the concentration of NaOH used is low, calcium dissolved from the GGBFS will take part in the formation of amorphous CSH gel, in preference to the formation of a calcium based geopolymer. CSH gel can be formed within a geopolymeric binder if soluble calcium is available in the mixture. However, if there is excess amount of hydroxides present in the system, the precipitation of calcium hydroxide will be promoted. Subsequently, the precipitation of calcium hydroxide will inhibit any possible formation of CSH gel within a geopolymeric binder unless a significant amount of calcium is present initially.

The strength development of the MK-GGBFS binder is an on-going process. However, strength development is highly dependent on the mass ratio between the MK and GGBFS. The optimum ratio between MK and GGBFS used is further
dependent on the alkaline condition used. It is suggested that the coexistence of geopolymeric gel and CSH gel is responsible for the strength increase in matrices containing a moderate amount of GGBFS. It is postulated that the formation of CSH gel within a geopolymeric binder acts as a micro-aggregate, such that the resultant binder is homogeneous and dense, resulting in increased mechanical strength with time. The microanalysis and the chemical mechanism behind the coexistence of the CSH and geopolymeric phases will be examined and discussed further in the next chapter.
Table 4.1: Chemical composition of metakaolin (MK) and ground granulated blast furnace slag (GGBFS)

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
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<tr>
<td>MK</td>
<td>0.10</td>
<td>54.78</td>
<td>40.42</td>
<td>0.76</td>
<td>0.41</td>
<td>2.72</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>GGBFS</td>
<td>43.0</td>
<td>34.4</td>
<td>14.1</td>
<td>0.11</td>
<td>6.3</td>
<td>0.33</td>
<td>0.3</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 4.2: Physical characteristics of metakaolin (MK) and ground granulated blast furnace slag (GGBFS).

<table>
<thead>
<tr>
<th></th>
<th>Mean¹</th>
<th>Mode¹</th>
<th>D₁₀¹</th>
<th>D₅₀¹</th>
<th>D₉₀¹</th>
<th>Bulk Density²</th>
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<tr>
<td></td>
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<td>(μm)</td>
<td>(μm)</td>
<td>(μm)</td>
<td>(μm)</td>
<td>(g/m³)</td>
</tr>
<tr>
<td>MK</td>
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<td>1.045</td>
<td>1.579</td>
<td>3.006</td>
<td>2.5</td>
</tr>
<tr>
<td>GGBFS</td>
<td>21.54</td>
<td>15.14</td>
<td>2.547</td>
<td>15.14</td>
<td>47.02</td>
<td>2.33</td>
</tr>
</tbody>
</table>

¹ Particle size distribution was determined by the Coulter LS130 particle sizer.
² As supplied by the manufacturer
Table 4.3: Composition of different matrices synthesised in this study\(^1\).

<table>
<thead>
<tr>
<th>Matrix</th>
<th>MK / (MK + GGBFS)</th>
<th>Ms = SiO(_2) / Na(_2)O (molar ratio)</th>
<th>(NaOH + NaSiO(_3)) / (MK + GGBFS) (mass ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>1</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M2</td>
<td>0.8</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M3</td>
<td>0.6</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M4</td>
<td>0.4</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M5</td>
<td>0.2</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M6</td>
<td>0</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>N1</td>
<td>1</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N2</td>
<td>0.8</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N3</td>
<td>0.6</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N4</td>
<td>0.4</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N5</td>
<td>0.2</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N6</td>
<td>0</td>
<td>1.2</td>
<td>1.63</td>
</tr>
</tbody>
</table>

\(^1\) The total molar content of H\(_2\)O and soluble silicate (from alkaline activator) in each matrix remained constant.
Table 4.4: Compressive strength of matrices synthesised using $M_s = 2.0$ and 
$\text{(NaOH+NaSiO}_3)/\text{(MK+GGBFS)} = 1.45$.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>MK / (MK + GGBFS)</th>
<th>Compressive Strength (MPa) with Time (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Mass Ratio)</td>
<td>1</td>
</tr>
<tr>
<td>M1</td>
<td>1</td>
<td>32.1</td>
</tr>
<tr>
<td>M2</td>
<td>0.8</td>
<td>39.3</td>
</tr>
<tr>
<td>M3</td>
<td>0.6</td>
<td>38.0</td>
</tr>
<tr>
<td>M4</td>
<td>0.4</td>
<td>31.4</td>
</tr>
<tr>
<td>M5</td>
<td>0.2</td>
<td>20.2</td>
</tr>
<tr>
<td>M6</td>
<td>0</td>
<td>8.9</td>
</tr>
</tbody>
</table>

a. Sample not tested.
Table 4.5: Compressive strength of matrices synthesised using $M_s = 1.2$ and 
$(\text{NaOH}+\text{NaSiO}_3)/(\text{MK}+\text{GGBFS}) = 1.63$.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>MK / (MK + GGBFS) (Mass Ratio)</th>
<th>Compressive Strength (MPa) with Time (Days)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N1</td>
<td>1</td>
<td>35.4</td>
</tr>
<tr>
<td>N2</td>
<td>0.8</td>
<td>32.8</td>
</tr>
<tr>
<td>N3</td>
<td>0.6</td>
<td>26.7</td>
</tr>
<tr>
<td>N4</td>
<td>0.4</td>
<td>20.3</td>
</tr>
<tr>
<td>N5</td>
<td>0.2</td>
<td>13.5</td>
</tr>
<tr>
<td>N6</td>
<td>0</td>
<td>14.1</td>
</tr>
</tbody>
</table>

a. Sample not tested.
b. Matrix fractured prior to strength test.
Table 4.6: The average elemental compositions (mol%) of Phases A and B as shown in Figure 4.20.

<table>
<thead>
<tr>
<th></th>
<th>Oxygen (O)</th>
<th>Sodium (Na)</th>
<th>Aluminium (Al)</th>
<th>Silicon (Si)</th>
<th>Calcium (Ca)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase A</td>
<td>65.9</td>
<td>8.55</td>
<td>7.42</td>
<td>16.2</td>
<td>1.12</td>
</tr>
<tr>
<td>Phase B</td>
<td>67.5</td>
<td>4.48</td>
<td>2.86</td>
<td>11.8</td>
<td>11.6</td>
</tr>
</tbody>
</table>
Figure 4.1. Conceptual mapping of the likely products resulting from the alkaline activation of an aluminosilicate in the presence of a calcium source.

Figure 4.2: X-ray diffractograms of raw metakaolin (MK) and ground granulated blast furnace slag (GGBFS).
Figure 4.3: Scanning electron micrograph of metakaolin (MetaStar 402).
Figure 4.4: Transmission electron micrograph of metakaolin used. This micrograph highlights the prominent hexagonal particles present in metakaolin.
Figure 4.5: Transmission electron micrograph of metakaolin used, where “A” represents the small percentage of the fibrillar structure present in metakaolin.

Figure 4.6: Transmission electron micrograph of kaolin (metakaolin before calcination). This micrograph highlights the regular hexagonal plate present in kaolin.
Figure 4.7: Scanning electron micrograph of ground granulated blast furnace slag (GBFS).
Figure 4.8: Compressive strength profile of matrices (Matrices M1 to M6) containing various amount of GGBFS synthesised using Ms = 2.0 (low alkaline).

Figure 4.9: Compressive strength profile of matrices (Matrices N1 to N6) containing various amount of GGBFS synthesised using Ms = 1.2 (high alkaline).
Figure 4.10: XRD diffractograms of matrices (M1 to M6) synthesised with the addition of various amount of ground granulated blast furnace slag (GGBFS) with alkaline activation (Ms = 2.0) at 28 days.

Figure 4.11: XRD diffractograms of matrices (N1 to N6) synthesised with the addition of various amount of ground granulated blast furnace slag (GGBFS) with alkaline activation (Ms = 1.2) at 28 days.
Figure 4.12: Highlighted region between 20° to 40° 2-theta of Figure 4.10.
Figure 4.13: Differences between the x-ray diffractogram of matrices (M1 to M6) before and after (28 days) alkaline activation (Ms = 2.0).

Figure 4.14: Differences between the x-ray diffractogram of matrices (N1 to N6) before and after (28 days) alkaline activation (Ms = 1.2).
Figure 4.15: XRD diffractograms of Matrix M2 at different ages.
Figure 4.16: Scanning electron micrograph of Matrix M1 (100% MK, Ms = 2.0) at 14 days.
Figure 4.17: Transmission electron micrograph of Matrix M1 at 28 days. A - undissolved metakaolin particle, B - undissolved metakaolin particle, C - crystalline aluminosilicate and D - amorphous aluminosilicate. (Original magnification: x22600)
Figure 4.18: Electron diffraction pattern of Particle “C” as shown in Figure 4.17, which is believed to be a crystalline or semi-crystalline sodium aluminosilicate. (CAM length = 1040 mm with a corresponding CAM constant = 35 and rotation of −92°).
Figure 4.19: Electron diffraction ring pattern of Particle "D" as shown in Figure 4.17, which is believed to be a semi-crystalline to amorphous constituent of a geopolymeric gel. (CAM length = 1040 mm with a corresponding CAM constant = 35 and rotation of −92°).
Figure 4.20: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 14 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 4.21: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 240 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 4.22: Transmission electron micrograph of Matrix M3 (40%GGBFS, Ms = 2.0) at 28 days. A - synthetic crystalline aluminosilicate (constituent of a geopolymeric binder), B - amorphous aluminosilicate and C - calcium silicate hydrate with a small proportion of aluminium. (Original magnification: x36300)
Figure 4.23: Electron diffraction of the crystalline phase present in Matrix M3 (40%GGBFS, Ms = 2.0) at 28 days. (CAM length = 1510mm with a corresponding CAM constant = 50.7 and rotation of −87°)
Figure 4.24: A common semi-crystalline phase (as shown with a defined electron diffraction ring pattern) present in the resultant binder with a substantial amount of GGBFS. This particular electron diffraction was taken for Matrix M5, 80% of GGBFS and Ms = 2.0 at 28 days. (CAM length = 1510mm with a corresponding CAM constant = 50.7 and rotation of −87°)
Figure 4.25: Scanning electron micrograph of Matrix M4 (60% slag, Ms = 2.0) at 14 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 4.26: Scanning electron micrograph of Matrix N4 (60% slag, $M_s = 1.2$) at 14 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 4.27: Scanning electron micrograph of Matrix N2 (20% slag, Ms = 1.2) at 14 days. A clear formation of CSH phase could not be observed in such binder; instead, scattering of small calcium precipitates (the white bright islands, <10μm) around the binder was observed.
Figure 4.28: Scanning electron micrograph of Matrix M5 (80% slag, Mₕ = 2.0) at 28 days. This highlights the morphology of crystalline calcium silicate hydrate structure formed. (Using a JEOL JSM-840 SEM machine)
Chapter 5

Microanalysis of Calcium Silicate Hydrate and Geopolymeric Gels within a MK-GGBFS System

Chapter 4 examined the physical and chemical mechanistic effects of granulated blast furnace slag (GGBFS) addition on geopolymerisation. It was found that the coexistence of geopolymeric and calcium silicate hydrate (CSH) gels was possible, however, it is highly dependent on the alkalinity of the alkaline activator and the mass ratio between metakaolin and GGBFS used in the synthesis. This chapter will focus on the microanalysis of the coexistence of these two phases.

Scanning electron microscopy was employed to study the morphology and elemental composition of the two phases. The elemental composition within the different phases was found to be consistent. However, it was found that the CSH gel formed in the system studied had a significantly lower Ca/Si ratio than the CSH commonly formed by the hydration of ordinary Portland cement (OPC). In addition, some calcium precipitate was observed at the interface between the CSH and geopolymeric gels. It is proposed that the properties (e.g. size, elemental composition) of the geopolymeric and CSH gels forming simultaneously, and the reactivity of the calcium precipitates along the interfacial region, will hold the key in reformulating a new generation of concrete that matches the durability of ancient concrete. The chemical mechanism of the alkaline activation of metakaolin (MK) in the presence of GGBFS is proposed in this chapter.

5.1 Background

As discussed in Chapter 2, the search for a new environmentally friendly construction material that will match the durability of ancient concrete has motivated the study of alkaline activated cementitious systems over the past three decades. In studying the durability of ancient construction material in comparison to their modern counterparts, it has been demonstrated by Glukhovsky that the hydration products of ancient concrete are not limited to the hydration of C₃S, C₂S, C₃A and C₄AF, but also include the hydration of low-basic alkaline or alkali-earth aluminosilicate systems (Glukhovsky, 1994). This low-basic alkaline aluminosilicate system could be viewed as the basic geopolymeric system (i.e. amorphous Na⁺ or K⁺ aluminosilicate network) commonly synthesised today (Krivenko, 1994).

Calcium silicate hydrate (CSH) gel and calcium hydroxide are commonly acknowledged to be the major hydration products of modern ordinary Portland cement (Taylor, 1964). Hitherto, no documented research has yet identified a system, in which both CSH gel and geopolymeric gel could be formed simultaneously within a single system based on the hydration process of ordinary Portland cement alone. The lack of durability in modern concrete in comparison to ancient concrete could be attributed to the inability of the modern cementitious system to form a product that consists of both CSH and geopolymeric gels. In order to understand the chemical mechanism behind the durability of ancient concrete, it is essential to reformulate a system that will favour the formation of both CSH and geopolymeric gels within a single system, so that a direct comparison can be made between ancient concrete and this new modern concrete. Subsequently, the microanalysis and the chemical mechanism responsible for the coexistence of both CSH and geopolymeric gels in enhancing the durability of the resultant binder is the focus of this chapter.

Calcium silicate hydrate is a gel of hydrated CaO-SiO₂, which is normally non-stoichiometric. As discussed in the previous chapters, it is generally agreed that CSH gel is the major component that contributes to the mechanical strength of cement (Taylor, 1964). In contrast, the formation of the three-dimensional amorphous alkali aluminosilicate network with a general formula of (Na₅K)ₙ-[Si-O₂]₂-Al-O]ₙ·wH₂O is
often argued to be the phase that gives the binding property to the geopolymeric gel (van Jaarsveld, 2000; Davidovits, 1999, 1991; Davidovits et al., 1990). The major difference between CSH gel and geopolymeric gel in terms of their elemental composition is calcium. It is anticipated that if enough calcium is added to a geopolymeric system, some forms of CSH gel will be obtained instead, however it is still unclear whether calcium will participate in geopolymerisation in a similar way to sodium or potassium (van Jaarsveld, 2000; Davidovits, 1999, 1991; Davidovits and Davidovics, 1988). As a result, an investigation into the role of calcium in dictating the chemical mechanism involved in geopolymerisation and formation of CSH gel will be essential in understanding how the coexistence of the two phases will benefit the properties of the resultant binder.

As described previously in Chapter 4, numerous studies have been conducted on various metakaolin (MK)/lime (calcium hydroxide) and MK-blended cement systems in recent years (Alonso and Palomo, 2001a, b; Cabrera and Rojas, 2001; Frias and Cabrera, 2001; Coleman and McWhinnie, 2000; Frias et al., 2000). It was found that various products such as CSH gel, geopolymeric gel, $C_2ASH_8$ (stratline) and $C_4AH_{13}$ (tetracalcium aluminate hydrate) could be synthesised depending on the alkalinity and the different ratios between the aluminosilicate and calcium sources used. In particular, it was found that it is possible to have geopolymeric and CSH gels forming simultaneously in a MK/lime system (Alonso and Palomo, 2001a, b).

This chapter focuses on a microscopic study conducted on a MK/GGBFS system. Chapter 4 has demonstrated that geopolymeric and CSH gels could be formed simultaneously in a lowly alkaline MK-GGBFS system. Moreover, it was found that the presence of both geopolymeric and CSH gels within a single binder increased the compressive strength and enhanced the durability of the resultant matrices. However, x-ray diffraction (XRD) alone was inconclusive to clearly define the structures of the two phases due to the highly amorphous nature of both raw MK and GGBFS, and the resultant product. The findings from the current microanalysis of such a system are fundamental to the understanding of the mechanistic relationships between geopolymers and CSH.
5.2 Experimental Procedure

Readers are advised to refer to Section 3.2 for a detailed description of the geopolymer sample synthesis. A description of all analytical techniques used in this chapter can be found in Section 3.4. The following section will therefore only highlight the information of most relevance to the current chapter.

A detailed SEM examination of the resultant specimen after the alkaline activation was conducted over the two different sets of matrices synthesised using different ratios of MK and GGBFS, and alkalinity as described in Section 4.2. Table 5.1 presents a summary of the matrices discussed in this chapter. Readers are advised to refer to Section 4.2 for a detailed description of the synthesis procedure and the general description of the raw MK and GGBFS used. The oxide compositions of MK and GGBFS are shown in Table 5.2, which were obtained by XRF analysis using a Siemens SRS 3000 instrument (Section 3.4.1). Table 5.3 presents the different molar ratios between the main oxides of interest in both MK and GGBFS.

As detailed in Section 3.4, a Philips XL30 scanning electron microscope, operated at 20keV was used in analysing the surface morphology of each specimen. EDS (Energy Dispersive Spectroscopy) was used to analyse the elemental composition of the surface of each specimen. A DYNAVAC sputter coater was used in coating each specimen with carbon. Elemental analysis was conducted randomly across the area of interest. The average value and standard deviation presented in this chapter were calculated using a computer software Microsoft © Excel 2000.

5.3 Results and Discussion

5.3.1 Microstructure and Hydration Products Synthesised at Ms = 2.0

Chapter 4 discussed a common microstructural feature found in the MK/GGBFS system synthesised at low alkalinity (Ms = 2.0), whereby two separate phases formed as a result of the alkaline activation of metakaolin in the presence of a moderate amount of GGBFS (Matrices M2 to M4). A SEM micrograph, which shows the formation of two distinct phases in Matrix M2, is presented in Figure 5.1.
As discussed in Section 4.3.5, EDS analysis was conducted on the binder in the two separate phases. The results have shown that the two phases had vastly different elemental composition, where one phase (Area A) consisted mainly of silicon, aluminium and sodium with about 1 mol% calcium, while the other phase (Area B) was found to be dominated by the presence of silicon and calcium with some sodium and less than 3 mol% aluminium. Based on the elemental composition of areas A and B, it is suggested that area A consisted mainly of a geopolymer gel, while some form of calcium silicate hydrate (CSH) gel as the main component in area B.

Figures 5.2 and 5.3 show the same binder (Matrix M2) at 240 days, where the coexistence of two separate phases remains as a prominent feature. These images illustrate that two separate phases (A and B) clearly coexist, however the boundary between the two phases become less well-defined with time (Figures 5.1 and 5.2). The phase composition of the resultant binder is suggested to move slowly towards a binder with a single homogeneous phase with time. The larger particles present in the calcium phases were found to have various compositions and are enlarged in Figure 5.3. These particles were of different size, morphology and with different elemental composition. These particles contained various precipitates, such as calcium hydroxide as well as unreacted MK or GGBFS particles.

The crystalline precipitated phases, such as calcium hydroxide and calcium aluminate, are expected to be of a very low quantity, therefore their presence cannot be detected using XRD as their crystalline peaks are of a very low intensity as described previously in Chapter 4. From the elemental analysis of the various particles formed within the calcium rich phase, the larger particles (e.g. particles “C” and “D” in Figure 5.4) had a substantially higher CaO/SiO$_2$ ratio than the smaller ones (e.g. particle “E”). The larger calcium particles tended to be situated along the interfacial region between the calcium rich region and the aluminosilicate rich region (Figures 5.1 and 5.2). In addition, it is thought that the presence of the large quantity of calcium along the interfacial region, could be the result of the precipitation of calcium hydroxide.

As more GGBFS was added to the system, the coexistence of geopolymeric gel and calcium silicate hydrate was still the prominent microscopic feature of the binders synthesised as shown in Figures 5.5 and 5.6. However a clear distinction between the
two phases could not be observed when more than 80 wt.% of GGBFS was used. The major products formed in a high percent GGBFS system were similar to that of alkaline activation of GGBFS alone (Matrix M6). Major products consist of various types of calcium phases, which are likely to include calcium silicate hydrate, calcium aluminate hydrate and calcium aluminosilicate hydrate as shown in Figure 5.7. However, due to the highly amorphous nature of these products, it was not possible to clearly identify the end products.

5.3.2 Microstructure and Hydration Products Synthesised at Ms = 1.2

The effect of increasing the concentration of sodium hydroxide on the microstructure of the resultant MK/GGBFS binder was discussed previously in Section 4.3.5, whereby Matrices N1 to N6 were synthesised with the same MK and GGBFS composition as Matrices M1 to M6, but at a lower SiO₂/Na₂O ratio (Ms = 1.2). It was found that the coexistence of two separate phases was no longer the dominant microscopic feature of the resultant binder, (as shown in the binder synthesised using Ms = 2.0), unless a substantial amount of GGBFS (Matrix N4) was used initially (Figure 5.8).

Therefore the major product formed at high alkalinity with <50 wt.% of GGBFS was a geopolymeric gel similar to the one formed at low alkalinity (Figure 5.1). As shown in Figure 5.9, the microscopic analysis on this system (Matrix N2) has also indicated that there are small calcium precipitates (<10μm) scattered around the sodium aluminosilicate phase. The absence of the formation of distinct CSH and geopolymer gels in such a system indicated that the phase coexistence is dependent on the alkalinity used as well as the ratio between GGBFS and MK.

The current microscopic analysis confirmed the previous findings by Alonso and Palomo (2001b), wherein it was reported that some forms of CSH gel were the main reaction products when metakaolin was alkaline activated in the presence of calcium hydroxide at low alkalinity. When the concentration of hydroxide was increased from 5M to 10M, an amorphous alkaline aluminosilicate (geopolymer) would be formed as the dominant product with a small amount of CSH gel also being formed.
The current system is more complex with an amorphous calcium mineral (GGBS) being used and soluble silicate source being added. Different glassy phases in GGBFS are expected to react at different rates. Moreover, the presence of minor elements, such as iron and sulphur could initiate other side reactions, resulting in the development of other minor products. Nevertheless, the results have reconfirmed that, provided the right conditions are present, the formation of geopolymeric and CSH gel can take place simultaneously in the same system.

5.3.3 Elemental Analysis Along the Interfacial Region Between Geopolymeric and CSH Gels

In order to understand the chemical mechanism responsible for the coexistence of geopolymeric and CSH gels, a linescan analysis (marked as x-y in Figure 5.1) detailing the changes in elemental composition was conducted across the two separate phases existing in Matrix M2. Figure 5.10 shows the processed elemental concentration profile across the region. The standard deviations in Table 5.4 based on the elemental compositions in Figure 5.10 show that the concentration of each element was consistent within areas A and B, and that there was a narrow interfacial area (z₁-z₂) between the two regions. Apart from calcium and oxygen, the concentrations of silicon, aluminium and sodium were more concentrated in the aluminosilicate rich area (Area A, x-z₁) than in the calcium rich area (Area B, z₂-y).

Figure 5.10 and Table 5.4 show that the molar concentration of calcium increased 15 fold in less than a distance of 50µm at the interfacial region. After a sharp increase in calcium concentration in the interfacial region, the concentration decreased to a lower but consistent level when it reached the bulk of area B. This indicates that not only the materials in areas A and B are vastly different, but also the calcium species in the interfacial region are substantially different from the CSH gel in the main body.

With the concentration of sodium in both raw materials being very low (<0.22 mol%, Table 5.4), it is expected that the sodium found in both phases originated from the alkaline activator (NaOH and Na$_3$SiO$_3$). The EDS analysis has shown that the sodium concentration in the geopolymeric gel was higher than that in the calcium rich area. This indicates that the sodium added had a more prominent structurally determining role in the aluminosilicate gel than for the CSH gel. This result is expected as sodium

The effect of alkali on ordinary Portland cement has been widely studied, partly due to the problems associated with the alkali-aggregate reaction and carbonation, which are believed to be some of the main causes of deterioration of modern concrete (Gani, 1997; Taylor, 1964). Xu and Sarkar (1991) found that some substitutions of sodium for calcium in CSH in a gypsum activated flyash system is possible, however, no documented research has confirmed that alkali will play a significant structurally determining role in forming CSH gel. The difference therefore in the sodium concentration has also suggested that the phases in areas A and B are different. The presence of sodium in the CSH gel phase is likely to result from a small extent of substitution of sodium for calcium in CSH and the formation of various sodium precipitates, e.g. sodium silicate, sodium carbonate, sodium sulphate and various forms of sodium aluminosilicate or aluminate.

The concentration of silicon did not vary much across the two phases, with the aluminosilicate gel having a higher silicon concentration than the calcium rich phase (Table 5.4 and Figure 5.10). The slightly higher concentration of oxygen in the calcium rich phase is suggested to be due to the presence of various forms of calcium silicate hydrate and calcium hydroxide in the region. The difference in aluminium concentration between the two regions was also significant.

By further analysis, it is found that the molar ratio between calcium and silicon in the calcium rich phase is about 1, while the molar ratio between the two species in the GGBFS is about 1.3 (Table 5.4). The molar ratio between aluminium and calcium in area B and that in raw GGBFS is 0.25 and 0.36 respectively. The difference between these ratios in the calcium rich phase and raw GGBFS grain, as well as the presence of sodium in the region, indicated that the calcium rich phase is not just a large area of unreacted GGBFS grains, rather that some new calcium hydrated phases are the main products in region B.
The rapid increase in calcium concentration and decrease in aluminium concentration from the geopolymeric gel (A) to the calcium rich region (B), has indicated that during alkaline activation, aluminium diffuses out of region B and participates in forming the aluminosilicate in region A. The diffusion of aluminium from area B to A is confirmed by the much lower Al:Ca ratio found in area B than in GGBFS grains. It is thought that dissolved calcium will bind with dissolved silicate preferentially in region B, which causes the dissolved aluminate species to diffuse out of area B and participate in the polymerisation with other silicate and aluminate dissociated from MK in forming the geopolymeric gel in Area A.

The calcium content in region A has a high standard deviation, and appears to be unevenly distributed, perhaps owing to a precipitated phase interspaced with the aluminosilicate. However, the standard derivations of the sodium, aluminium and silicon concentration are greater in region B than in A. This suggests that the calcium rich region consists of a greater variety of phases than the aluminosilicate region.

The atomic ratio between silicon and aluminium was slightly higher than 2, while the ratio between sodium and aluminium was slightly greater than 1 for the aluminosilicate region. According to the chemical designation of geopolymers as suggested by Davidovits (Davidovits, 1999), the resultant aluminosilicate phase formed in this binder (Matrix M2) would be similar to the poly(sialate-siloxo) $M_a-(Si-O-Al-O-Si-O)_n$ with Si:Al = 2:1 and Na:Al = 1:1. According to Davidovits (Davidovits, 1999), this type of geopolymer results from the chemical reaction at atmospheric pressure of geopolymeric precursors such as aluminosilicate oxides (Al$^{3+}$ in IV-fold coordination) with alkaline polysilicate yielding polymeric Si-O-Al bonds. The conditions used in forming poly(sialate-siloxo) are similar to those used in synthesising the binders in the current study. Apart from the presence of a low percentage of calcium within area A, the aluminosilicate gel formed appears to be similar to the standard poly(sialate-siloxo). Therefore, despite the addition of moderate amounts of GGBFS, the geopolymers were still the main products formed as a result of the alkaline activation of MK. However, it is inconclusive at this stage to suggest the type of bonding between calcium and the aluminosilicate based on the SEM examination alone. It is unlikely that calcium will form a charge-balancing role in the same way as the sodium, as it is believed that calcium will form calcium
hydroxide and calcium silicate preferentially. The presence of calcium is suggested to be the result of the formation of calcium precipitates or the presence of undissolved GGBFS within the geopolymeric gel.

5.3.4 Microanalysis of Hydration Products

The elemental analyses of the different gel phases of the binders synthesised at Ms = 2.0 and 1.2 at 14 days are summarised in Tables 5.5 and 5.6. It should be noted that there was no clear phase separation occurring in some MK/GGBFS systems (namely Matrices M5, N2 and N3), so that the elemental analyses of the different gel phases for these matrices were estimated from areas with substantial difference in the concentration of calcium.

From Tables 5.5 and 5.6, it can be seen that the average composition of the aluminosilicate gel changed from Na_{0.53}Ca_{0.07}SiAl_{0.46} (20% GGBFS) to Na_{1.7}Ca_{0.25}SiAl_{0.24} (80% GGBFS) for Ms = 2.0, and from Na_{0.89}Ca_{0.05}SiAl_{0.46} (20% GGBFS) to Na_{1.7}Ca_{0.25}SiAl_{0.24} (80% GGBFS) for Ms = 1.2. Moreover, it can be observed that the Al_{2}O_{3}/SiO_{2} (A/S) ratio of the aluminosilicate rich gel decreased as the GGBFS content increased. This trend is expected as most aluminium originated from MK, so that as the MK/(MK+GGBFS) ratio decreased (i.e. increased addition of GGBFS), the amount of aluminium present in the system also decreased accordingly.

In addition, the Na:Si and Ca:Si ratios increased as the aluminium content decreased in the aluminosilicate rich phase. This may be due to excess silicate in the aluminosilicate rich phase resulting from the lack of aluminium available for polymerisation. It is possible that the lack of dissolved aluminium species in the solution phase has hindered any further formation of large silicate oligomers. The demand for calcium and sodium within the structure increases in order to balance the negative charge within the shorter silicates chain.

As the amount of sodium hydroxide is increased in the system, it would be expected that less calcium would be available to react with the silicate and aluminate. This is because calcium would precipitate as calcium hydroxide, rather than forming CSH gel as discussed in Section 4.3.2. It has been confirmed in the current study by the
microscopic and elemental analysis along the interfacial region between the two phases that various calcium precipitates are formed.

The CaO/SiO₂ (C/S) molar ratios of CSH gel in most kinds of cementitious systems have been well studied using different techniques such as phase equilibrium, extraction techniques and analytical electron microscopy (Lundgaard and Jons, 2003; Escalante-Garcia et al., 1999; Faucon et al., 1999, 1997). There are a large number of crystalline, semi-crystalline and amorphous CSH phases possible as a result of the hydration of cement (Taylor, 1964). Taylor (1964) argued that the complexity of the CaO-SiO₂-H₂O system lies in the greater ionic radius and more electropositive character of calcium, which permits different types of coordination with oxygen.

Tables 5.5 and 5.6 show that the molar ratios between calcium, silicon, aluminium and sodium varied according to the mass ratios of MK to GGBFS in the system initially. For matrices M1 to M6 synthesised at Ms = 2.0 (Table 5.5), the C/S ratios of the calcium rich phase were relatively consistent, increasing from ~0.9 to ~1.2. As a general trend, the C/S ratio increased with increasing GGBFS content in the binder. The same trend was observed in the C/S ratios in the aluminosilicate rich phase and also in the corresponding ratios for matrices synthesised using Ms = 1.2 (Table 5.6).

Richardson (1999) found that the C/S ratio of CSH in ordinary Portland cement pastes varies from ~1.2 to ~2.3 with a mean of ~1.75. These numbers are higher than those found in the current work. It is therefore concluded that the nature of calcium silicate hydrates formed in the binders studied was different from the normal CSH gel formed in Portland cement and also the amorphous calcium silicate present in raw slag. However, as the alkalinity of the alkaline activator decreased, the characteristics of the CSH gel formed appear to increasingly resemble the CSH in Portland cement.

Table 5.6 shows that for the calcium rich phase synthesised at high alkalinity (Ms = 1.2) and with moderate amounts of GGBFS (Matrices N2 and N3) the Al₂O₃/Na₂O ratios were substantially higher than in the other matrices studied. The values are also considerably higher than those determined for the Al-rich phase. It is suggested that the high aluminium content results from a high concentration of unreacted GGBFS grains present in the region. Subsequently, it is anticipated that the presence of a large
amount of sodium hydroxide could inhibit the possible formation of calcium silicate hydrate. A detailed discussion on the effect of excess sodium hydroxide in inhibiting the growth of CSH gel will be presented in the following section.

5.3.5 Proposed Mechanism of Alkaline Activation of MK in the Presence of GGBFS

It is found in the current work that the alkaline activation of MK in the presence of GGBFS is highly dependent on the alkalinity of the alkaline activator and the ratio between MK and GGBFS. The microscopic analysis has shown that given the right synthesis conditions, two separate phases (a calcium silicate phase and a sodium aluminosilicate gel) will form simultaneously in the alkaline activation process.

It is often argued that dissolution of aluminosilicate minerals is the first step of geopolymerisation (Xu and van Deventer, 2000; Krivenko, 1994). The TEM study conducted on the alkaline activation of MK, as shown in Section 4.3.4, has confirmed that the partial dissolution of the aluminosilicate material is the first mechanistic step of geopolymerisation. In the current study, it is thought that when both MK and GGBFS are mixed with the alkaline activator (sodium hydroxide and sodium silicate solution), dissolution is also the first reaction to take place. Silicon and aluminium will be dissolved from the surface of MK and at the same time silicon, aluminium and calcium will be dissolved from the surface of GGBFS. The rate of dissolution from each mineral is dependent on the concentration of sodium hydroxide and the particle size used. Therefore, it is anticipated that the dissolution rate of MK and GGBFS at different alkalinity will determine the ratios of the dissolved species present in the system. The nature and amount of dissolved species present in the suspension will determine the subsequent reaction or reactions to take place, which are expected to include polymerisation and various other precipitation processes.

When the alkaline solution activates the surface of the GGBFS, calcium and silicon dissolve from the GGBFS surface. It was found from the current study that dissolved calcium from GGBFS would take part in the formation of CSH gel or other calcium-containing species in preference to participating in the polymerisation with aluminosilicate. It can be concluded that dissolved calcium from GGBFS plays a similar role to the calcium hydroxide as suggested by Alonso and Palomo (2001a, b),
i.e. the alkaline activation of MK, in the presence of Ca(OH)$_2$ leads to the formation of amorphous and semi-crystalline sodium aluminosilicate with some form of CSH gel as a secondary product. A schematic representation of the proposed chemical mechanism for the coexistence of geopolymer and CSH phases is presented in Figure 5.11.

In the presence of aqueous sodium hydroxide, the surface of GGBFS particles will be saturated with hydroxyl ions (Step II in Figure 5.11). It is thought that when calcium dissolves from GGBFS, it will diffuse out of the GGBFS grain (Step III in Figure 5.11) and will further react with hydroxyl ions and precipitate as Ca(OH)$_2$ (Step III in Figure 5.11). When there is a substantial amount of calcium hydroxide present around the surface of GGBFS, it will make the diffusion of calcium out of the GGBFS more difficult. Since the diffusion of calcium from GGBFS to aluminosilicate is restricted (Step V in Figure 5.11), excess calcium will remain intact within the GGBFS grain and form a new nucleation centre, in which amorphous calcium silicate hydrate will be produced (Step VI in Figure 5.11). The lack of dissolved calcium present in the aluminosilicate body will inhibit any formation of calcium aluminosilicate hydrate. It is suggested that the presence of the small amount of dissolved calcium will react with soluble silicate and precipitate only on the outer layer of a geopolymeric gel (ie. not from within the geopolymer gel itself). As a result, two distinct phases will be produced in such a system and substantial amounts of calcium hydroxide or various other types of calcium precipitate will be formed along the interfacial area as shown in the current investigation (Step VII in Figure 5.11).

At lower NaOH concentrations (~2.5M), layers of hydroxyl ions and calcium hydroxide will not be too thick along the interfacial area, so that a small amount of dissolved calcium will be able to diffuse out of the layers if there is a relatively high amount of dissolved calcium present in the system. Tables 5.5 and 5.6 show that in general the CaO/SiO$_2$ ratios of the rich aluminosilicate phase were slightly higher in matrices synthesised under Ms = 2.0.

Phair et al. (2000) showed that the solubility of calcium decreased with increasing pH owing to the formation of calcium hydroxide. With a decreased amount of calcium
hydroxide formed in the system at low alkalinity (Ms = 2.0), more calcium will be available to react with soluble silicate to form calcium silicate hydrate. Moreover, previous findings by Xu and van Deventer (2000) showed that the dissolution of silicon and aluminium from various aluminosilicate minerals is slower in an alkaline activator of a lower hydroxide concentration. Hence the formation of calcium silicate hydrate is favoured as the initial amount of dissolved aluminate is not enough to promote the formation of calcium aluminosilicate. In addition, since the layers of hydroxyl ions and calcium hydroxides species around the surface of the rich calcium silicate region are less rigid, more space is available for the nucleation growth of CSH in the region. Thus, the growth of CSH will be promoted and a clear region of calcium rich area could be distinguished using SEM (Figure 5.1).

In contrast, when more sodium hydroxide is added to the system (Ms = 1.2), only a limited amount, if any, of dissolved calcium species will participate in the formation of CSH, which makes its presence difficult to be observed using SEM. Instead, calcium hydroxide will precipitate, and this will limit the possibility for dissolved calcium to participate in the formation of CSH. A schematic representation of the alkaline activated MK-GGBFS system at high alkalinity is presented in Figure 5.12. With decreasing amounts of dissolved calcium present, the formation of CSH gel is not possible unless a higher amount of calcium source is added to the system initially. Therefore, when more GGBFS was added in the current study (> 60% by mass), a clear coexistence of the two phases could be observed (Figure 5.8). Moreover, as the layers of calcium hydroxide and hydroxyl ions are much thicker in systems of high alkalinity, the lack of physical space around the GGBFS grain has also restricted any possible growth of CSH (Steps IX and X in Figure 5.12). Subsequently, scattering of small calcium precipitates (<10μm) around the sodium aluminosilicate phase was observed in this study (Step XI in Figure 5.12). This may also explain why more unreacted GGBFS was observed in Matrices N2 and N3.

5.3.6 Effect of the Coexistence of Geopolymeric Gel and Calcium Silicate Hydrate on the Durability of Resultant Binder

The results of the current study have shown that given the right conditions, it is possible to have both amorphous alkaline aluminosilicate and CSH gel forming simultaneously within the same system. As suggested by Glukhovsky (1994), the
long-term stability of concrete results from the presence of analcime (alkaline silico-
aluminohydrates) and CSH gel rather than CSH gel alone. It is suggested that
analcime is similar to the alkali aluminosilicate (geopolymer) produced as a result of
the alkaline activation of MK. If the hypothesis of Glukhovsky is correct, then the
binder formed in the current work, with the coexistence of both geopolymeric and
CSH phases, will be the modern version of ancient concrete.

The alkaline activation of MK in the presence of a calcium source causes the two
reactions to take place simultaneously. It is anticipated that the amount, nature and
size of the two phases present will determine the initial mechanical properties of the
resultant matrices. The amount, nature and size of the hydration products can be
controlled by using different types of aluminosilicate and calcium source, different
ratios between aluminosilicate and calcium source, and a different type and quantity
of alkaline activator.

It was previously shown in Chapter 4 that the addition of excessive amounts of
GGBFs has a negative effect on the mechanical properties of the resultant binders.
Therefore, even though it is possible to form CSH and geopolymeric gels
simultaneously in a highly alkaline system (Ms = 1.2) by adding substantial amounts
of GGBFs as shown in this study, the mechanical properties of the resultant binder
may not necessarily be improved. It is suggested that the presence of unstable phases
such as calcium hydroxide and various other calcium precipitates along the interfacial
area will hold the key to the long-term durability of the resultant binder. It is
hypothesised that the presence of these precipitates will further promote reactions
between the geopolymeric gel and CSH gel, and that these reactions will determine
the durability of the binder.

Further evidence from SEM analysis (Table 5.7, Figures 5.2 and 5.3) supports this
hypothesis. As discussed earlier in Section 5.3.1, despite the coexistence of
gopolymeric and CSH gels even at 240 days (Figures 5.2 and 5.3), the boundary
between these two phases has become less defined with time as evidenced when
Figure 5.2 is compared to Figure 5.1. EDS analysis of the two phases at different age
confirms the ratios between the different oxides, in particular the molar ratio between
CaO and SiO₂, in both phases change with time as shown in Table 5.7. The difference
between the CaO/SiO$_2$ ratios in the two phases decreases with time; thereby indicating that further interaction between these two phases does take place.

It is suggested that the system is slowly transforming into a homogeneous system consisting of both geopolymer and CSH gels interlocking within its structure, with the consumption of the unstable (reactive) calcium species such as calcium hydroxide. Eventually, the clearly identifiable interface between geopolymeric and CSH gels should “disappear” and it may become difficult to identify the presence of the two phases on the micro-scale after an extended period of time. In contrast to the significant changes to the CaO/SiO$_2$ ratio with time, Al$_2$O$_3$/Na$_2$O and Al$_2$O$_3$/SiO$_2$ ratios remain relatively constant with age. This indicates that the overall structure of geopolymeric and CSH gels remains relatively unchanged, with geopolymeric gel still consisting of an alkaline aluminosilicate product that resembles poly(sialate-siloxo) with a similar Si/Al ratio as described earlier in Section 5.3.3. The presence of calcium in the geopolymeric gel is suggested to be the result of the presence of calcium silicate or calcium aluminate species interlocking within the geopolymeric structure. The resultant geopolymeric binder is thus stronger and more durable with time, similar to ancient concrete, as evidenced from the trends observed in the compressive strength as shown previously in Chapter 4.

5.4 Conclusion

It is suggested that the properties (e.g. size, elemental composition) of geopolymeric and CSH gels formed simultaneously in a MK-GGBFS system, and the reactivity of the interfacial zone between the two phases, will hold the key in reformulating a new generation of concrete that matches the durability of ancient concrete. CSH gel formed in such a system was found to have a significantly lower Ca/Si ratio than the CSH commonly formed from the hydration of ordinary Portland cement, while the geopolymeric gel formed was found to have similar aluminosilicate structure as that in the well-defined in poly(sialate-siloxo) geopolymer proposed by previous research.

With the consumption of the reactive species along the interfacial area with time, it is proposed that the system will slowly transform into a stable homogeneous binder.
consisting of both geopolymeric and CSH phases interlocking within the structure. The resultant binder will therefore be stronger and more durable with time, similar to ancient concrete. A chemical mechanism has been proposed on how the presence of GGBFS in the alkaline activation of MK could result in the formation and coexistence of two separate phases – geopolymeric gel and CSH gel.

Chapters 4 and 5 have so far discussed the physical and chemical effect of GGBFS, an amorphous calcium silicate material, on the role of calcium in a MK-based geopolymeric system. The next chapter will examine the effect of calcium silicate sources of different mineralogy on the role of calcium in geopolymerisation.
Table 5.1: Composition of geopolymer matrices.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>MK / (MK + GGBFS) (mass ratio)</th>
<th>Ms = SiO₂ / Na₂O (molar ratio)</th>
<th>(NaOH + NaSiO₃) / (MK + GGBFS) (mass ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>1</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M2</td>
<td>0.8</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M3</td>
<td>0.6</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M4</td>
<td>0.4</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M5</td>
<td>0.2</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>M6</td>
<td>0</td>
<td>2.0</td>
<td>1.45</td>
</tr>
<tr>
<td>N1</td>
<td>1</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N2</td>
<td>0.8</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N3</td>
<td>0.6</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N4</td>
<td>0.4</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N5</td>
<td>0.2</td>
<td>1.2</td>
<td>1.63</td>
</tr>
<tr>
<td>N6</td>
<td>0</td>
<td>1.2</td>
<td>1.63</td>
</tr>
</tbody>
</table>
Table 5.2: Chemical composition (mass %) of metakaolin (MK) and ground granulated blast furnace slag (GGBFS).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>0.10</td>
<td>54.78</td>
<td>40.42</td>
<td>0.76</td>
<td>0.41</td>
<td>2.72</td>
<td>0.07</td>
<td>--</td>
</tr>
<tr>
<td>GGBFS</td>
<td>43.0</td>
<td>34.4</td>
<td>14.1</td>
<td>0.11</td>
<td>6.3</td>
<td>0.33</td>
<td>0.3</td>
<td>0.58</td>
</tr>
</tbody>
</table>

Table 5.3: Elemental analysis (molar ratio) of metakaolin (MK) and ground granulated blast furnace slag (GGBFS).

<table>
<thead>
<tr>
<th>Molar Ratio</th>
<th>CaO/SiO₂</th>
<th>Al₂O₃/SiO₂</th>
<th>CaO/Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>0.002</td>
<td>0.43</td>
<td>0.0045</td>
</tr>
<tr>
<td>GGBFS</td>
<td>1.34</td>
<td>0.24</td>
<td>5.56</td>
</tr>
</tbody>
</table>
Table 5.4: EDS line-scan analysis (atomic%, $x \pm \sigma_{n,1}$) for the interface between the aluminosilicate rich phase and the calcium rich phase (Line x-y) as shown in Figure 5.1. ($x =$ average atomic %, $\sigma =$ standard deviation in %, and $n =$ number of sample size). The molar compositions of MK and GGBFS are also shown, based on Tables 5.2 and 5.3.

<table>
<thead>
<tr>
<th>Mole %</th>
<th>Oxygen (O)</th>
<th>Sodium (Na)</th>
<th>Aluminium (Al)</th>
<th>Silicon (Si)</th>
<th>Calcium (Ca)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall (x-y)</td>
<td>66.5±7.3%</td>
<td>4.64±33%</td>
<td>3.99±97%</td>
<td>13.2±40%</td>
<td>9.98±91%</td>
<td>256</td>
</tr>
<tr>
<td>Al-Si Region</td>
<td>65.9±5.5%</td>
<td>8.55±18%</td>
<td>7.42±26%</td>
<td>16.2±23%</td>
<td>1.12±71%</td>
<td>101</td>
</tr>
<tr>
<td>(x-z₁)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Interfacial</td>
<td>66.1±12%</td>
<td>4.52±31%</td>
<td>3.84±56%</td>
<td>12.5±47%</td>
<td>17.0±44%</td>
<td>12</td>
</tr>
<tr>
<td>Region (z₁-z₂)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rich Calcium</td>
<td>67.5±5.9%</td>
<td>4.48±36%</td>
<td>2.86±39%</td>
<td>11.8±37%</td>
<td>11.6±37%</td>
<td>143</td>
</tr>
<tr>
<td>Region (z₂-y)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MK¹</td>
<td>63.2</td>
<td>0.05</td>
<td>16.3</td>
<td>18.8</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>GGBFS¹</td>
<td>58.3</td>
<td>0.22</td>
<td>6.41</td>
<td>13.3</td>
<td>17.8</td>
<td></td>
</tr>
</tbody>
</table>

¹ Molar composition as calculated from Table 5.2.
Table 5.5: SEM EDS analysis (atomic ratios, \( x \pm \sigma_{n-1} \)) for rich aluminosilicate phase and rich calcium phase in MK-GGBFS binders at 14 days, synthesised using Ms = 2.0 (low alkalinity). (\( x \) = average atomic %, \( \sigma \) = standard deviation in % and \( n \) = number of sample size)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Matrix</th>
<th>( \text{CaO} / \text{SiO}_2 )</th>
<th>( \text{Al}_2\text{O}_3 / \text{Na}_2\text{O} )</th>
<th>( \text{Al}_2\text{O}_3 / \text{SiO}_2 )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rich Calcium Phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>0.99±2.8%</td>
<td>0.88±10%</td>
<td>0.12±17%</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>0.96±3.7%</td>
<td>0.79±12%</td>
<td>0.12±24%</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>0.91±5.3%</td>
<td>0.42±18%</td>
<td>0.10±7.8%</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>M5</td>
<td>1.12±11%</td>
<td>0.21±78%</td>
<td>0.14±39%</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>1.20±20%</td>
<td>0.19±110%</td>
<td>0.10±41%</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td><strong>Rich Aluminosilicate Phase</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M1</td>
<td>0</td>
<td>0.85±7.0%</td>
<td>0.26±6.6%</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>M2</td>
<td>0.07±26%</td>
<td>0.87±14%</td>
<td>0.23±15%</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>0.08±36%</td>
<td>0.97±54%</td>
<td>0.21±28%</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>M4</td>
<td>0.15±21%</td>
<td>0.54±16%</td>
<td>0.16±7.0%</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>M5</td>
<td>0.48±46%</td>
<td>0.21±140%</td>
<td>0.12±27%</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>M6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

1 Addition of GGBFS (mass %) increases from Matrix M1 to Matrix M6.
Table 5.6: SEM EDS analysis (atomic ratios, x±σ_{x-1}) for rich aluminosilicate phase and rich calcium phase in MK-GGBFS binders at 14 days, synthesised using Ms = 1.2 (high alkalinity). (x = average atomic %, σ = standard deviation in % and n = number of sample size)

<table>
<thead>
<tr>
<th>Matrix</th>
<th>CaO / SiO₂</th>
<th>Al₂O₃ / Na₂O</th>
<th>Al₂O₃ / SiO₂</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rich Calcium Phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>N2</td>
<td>1.00±25%</td>
<td>2.40±21%</td>
<td>0.23±7.8%</td>
<td>15</td>
</tr>
<tr>
<td>N3</td>
<td>0.97±16%</td>
<td>1.65±7.8%</td>
<td>0.21±8.6%</td>
<td>15</td>
</tr>
<tr>
<td>N4</td>
<td>1.01±1.8%</td>
<td>0.25±40%</td>
<td>0.10±26%</td>
<td>50</td>
</tr>
<tr>
<td>N5</td>
<td>1.11±4.9%</td>
<td>0.22±40%</td>
<td>0.10±7.2%</td>
<td>50</td>
</tr>
<tr>
<td>N6</td>
<td>1.19±1.6%</td>
<td>0.20±38%</td>
<td>0.10±15%</td>
<td>50</td>
</tr>
<tr>
<td>Rich Aluminosilicate Phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N1</td>
<td>0</td>
<td>0.73±12%</td>
<td>0.35±2.3%</td>
<td>45</td>
</tr>
<tr>
<td>N2</td>
<td>0.05±39%</td>
<td>0.51±19%</td>
<td>0.23±15%</td>
<td>60</td>
</tr>
<tr>
<td>N3</td>
<td>0.04±70%</td>
<td>0.29±32%</td>
<td>0.15±26%</td>
<td>55</td>
</tr>
<tr>
<td>N4</td>
<td>0.23±22%</td>
<td>0.32±3.7%</td>
<td>0.15±39%</td>
<td>48</td>
</tr>
<tr>
<td>N5</td>
<td>0.25±63%</td>
<td>0.15±14%</td>
<td>0.12±30%</td>
<td>45</td>
</tr>
<tr>
<td>N6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 Addition of GGBFS (mass %) increases from Matrix M1 to Matrix M6.
Table 5.7: SEM EDS analysis (atomic ratios, $x \pm \sigma_{n-1}$) of rich aluminosilicate phase and rich calcium phase of Matrix M2 at 14 and 240 days of synthesis respectively. ($x$ = average atomic %, $\sigma$ = standard deviation in % and $n$ = number of sample size).

<table>
<thead>
<tr>
<th></th>
<th>Rich Aluminosilicate Phase (A)</th>
<th>Rich Calcium Phase (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>14 day$^1$</td>
<td>240 day$^1$</td>
</tr>
<tr>
<td>CaO/SiO$_2$</td>
<td>0.07±26%</td>
<td>0.17±30%</td>
</tr>
<tr>
<td>Al$_2$O$_3$/Na$_2$O</td>
<td>0.87±14%</td>
<td>1.42±18%</td>
</tr>
<tr>
<td>Al$_2$O$_3$/SiO$_2$</td>
<td>0.23±15%</td>
<td>0.26±20%</td>
</tr>
</tbody>
</table>

1 Time (day) after synthesis.
Figure 5.1: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 14 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium. An elemental line-scan was conducted on x-y (See Figure 5.10). The interfacial region is marked z₁-z₂.
Figure 5.2: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 240 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 5.3: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 240 days. A - geopolymeric binder with low content of calcium; B - calcium silicate hydrate with a small proportion of aluminium.
Figure 5.4: Scanning electron micrograph of Matrix M2 (20% slag, Ms = 2.0) at 240 days, showing magnification of area B in Figure 5.3. The particle marked C is identified as a type of calcium silicate with some aluminium in its composition (CaO/SiO$_2$ = 1.32, Al$_2$O$_3$/Na$_2$O = 2.5 and Al$_2$O$_3$/SiO$_2$ = 0.2) with particle size in the range of 30-50µm. The particle marked D is identified as some form of calcium silicate with some aluminium in its composition (CaO/SiO$_2$ = 1.8, Al$_2$O$_3$/Na$_2$O = 2.0 and Al$_2$O$_3$/SiO$_2$ = 0.2) with size in the range of 20-30µm. The calcium content in particles similar to “D” is more than in “C”. The particle marked “E” is identified as some form of alumino-silicate with traces of calcium in its composition (CaO/SiO$_2$ = 0.43, Al$_2$O$_3$/Na$_2$O = 2.3 and Al$_2$O$_3$/SiO$_2$ = 0.26) with size of about 5µm.
Figure 5.5: Scanning electron micrographs of Matrix M4 (60% slag, Ms = 2.0) at 14 days. A clear coexistence of both geopolymer and CSH phases is the dominant feature. A – mainly geopolymeric phase; B – mainly calcium silicate hydrate phase.
Figure 5.6: Scanning electron micrographs of Matrix M4 (60% slag, Ms = 2.0) at 240 days. A clear coexistence of both geopolymer and CSH phases is the dominant feature. A – mainly geopolymeric phase; B – mainly calcium silicate hydrate phase.
Figure 5.7: Scanning electron micrographs of Matrix M6 (100% slag, Ms = 2.0) at 240 days. Various calcium phases with different elemental composition were observed, including calcium silicate hydrate.
Figure 5.8: Scanning electron micrograph of Matrix N4 (60% slag, Ms = 1.2) at 14 days. A – mainly geopolymeric phase; B – calcium silicate hydrate with a small proportion of aluminium.
Figure 5.9: Scanning electron micrograph of Matrix N2 (20% slag, Ms = 1.2) at 14 days. A clear CSH phase could not be observed, instead scattering of calcium precipitates (bright white areas, marked “F”, <10µm) was observed.
Figure 5.10: An elemental line-scan on x-y in Figure 5.1 with Figure 5.10a showing the mass composition and Figure 5.10b showing the atomic composition.
Figure 5.11: A schematic representation of the chemical mechanism proposed for the coexistence of geopolymeric and CSH gels in an alkaline activated MK-GGBFS system at low alkalinity.
Figure 5.12: A schematic representation of the chemical mechanism in an alkaline activated MK-GGBFS system at high alkalinity.
Chapter 6

Effect of Various Calcium Silicate Materials on Geopolymerisation

Chapters 4 and 5 have discussed the physical and chemical effects of ground granulated blast furnace slag (an amorphous calcium silicate source), on the role of calcium in a metakaolin (MK) based geopolymeric system. The chemical mechanistic interpretation of the coexistence of geopolymeric and calcium silicate hydrate (CSH) gels in a MK-GGBFS system has been proposed and discussed in Chapter 5. This chapter will focus on the effect of calcium silicate sources of different mineralogy on the role of calcium in geopolymerisation. Most importantly, how the mineralogical composition of different calcium silicate sources affects the mechanistic path of calcium in a MK-based geopolymeric system will be investigated.

Seven different calcium silicate materials have been studied in this chapter. It is found that at low alkalinity, the compressive strength of matrices prepared with predominantly amorphous calcium silicates is much higher than in the case of crystalline materials. The compressive strength of matrices containing natural calcium silicates improves with increasing concentration of sodium hydroxide, however the converse is observed in matrices synthesised with processed calcium silicate sources. Moreover, the difference in the compressive strength between matrices synthesised from different calcium silicate sources is significantly reduced at high alkalinity. Natural calcium silicates are unable to produce enough dissolved calcium species to generate sufficient calcium silicate hydrate to coexist with the geopolymeric gel. This is suggested as the reason behind the poor mechanical properties of such matrices. At high alkalinity, it is proposed that calcium will play a lesser role in affecting the nature of the end product, thus the extent of dissolution of calcium species from the different calcium silicate sources will not have a major impact on the resultant mechanical properties of the matrices. Subsequently, the
compressive strengths of the matrices synthesised at high alkalinity are found to be comparable.

(The work presented in this chapter is based on the manuscript: C.K. Yip, G.C. Lukey and J.S.J. van Deventer, “Effect of Various Calcium Silicate Materials on Geopolymerisation,” Cement and Concrete Research, Accepted 2004).

6.1 Background

Chapters 4 and 5 have shown that calcium, originating from an amorphous calcium silicate source, has a positive effect on the resultant mechanical properties of the geopolymeric binder. It was suggested that the moderate addition of calcium from ground granulated blast furnace slag (GGBFS) in a mildly alkaline condition would initiate the formation of calcium silicate hydrate (CSH) gel coexisting with a geopolymeric gel. The CSH gel formed in such system was also found to have a significantly lower Ca/Si ratio than the CSH commonly formed from the hydration of ordinary Portland cement, while the geopolymeric gel formed was found to have similar aluminosilicate structure as a poly(sialate-siloxo), as shown in Section 5.3.3. It was proposed that the formation of both geopolymeric and CSH gels within a single binder would improve the mechanical property and enhance the durability of the resultant binder that will match ancient concrete. It is however still unclear whether all calcium sources will behave similarly in a MK-based geopolymeric system, or whether the proposed theories and observations in previous chapters would only be applicable to calcium originating from an amorphous calcium silicate source, similar to GGBFS. This chapter, therefore, focuses on the effect of the mineralogical composition of the calcium silicate source on the role of calcium in geopolymerisation.

An understanding of the mechanisms that govern the geopolymerisation process is essential to understand fully how geopolymeric and calcium silicate hydrate gels could interact with each other. It is generally believed that there are three mechanistic steps: (1) dissolution, (2) transportation or orientation and (3) polycondensation (reprecipitation) involved in geopolymerisation (Xu et al., 2001; van Jaarsveld, 2000; Xu and van Deventer, 2000; Krivenko, 1994). It was also suggested in Chapter 5 that
when both MK and GGBFS are mixed with an alkaline activator, dissolution is also the first reaction to take place. However, it is still unknown how the mineralogical composition would affect the dissolution of calcium and silicon dissolving from the surface of different calcium silicate sources and their subsequent mechanistic path.

In the current study, seven different calcium silicate materials were added to a calcium-free geopolymeric binder synthesised by the alkaline activation of metakaolin (MK). The seven different calcium silicate sources used cover a range of natural calcium silicate minerals and two commonly used industrial materials, i.e. ground granulated blast furnace slag (GGBFS) and cement. This chapter will focus on the interrelationship between the dissolution rate of the different species in the original calcium silicate materials under different alkaline conditions, and the mechanical properties and nature of the resultant geopolymer products.

6.2 Experimental Procedure

Section 3.2 gives a detailed description of the geopolymer sample synthesis. A description of all analytical techniques used in this chapter can be found in Section 3.4.

6.2.1 Materials

Seven different calcium silicate (CS) sources were used in this study, and they are ground granulated blast furnace slag (GGBFS), cement (CEM), wollastonite (WOL), anorthite calcium plagioclase (ANO), hornblende (HRN), prehnite (PRN) and tremolite (TRM). GGBFS was obtained from Independent Cement, Melbourne, Australia. Cement was obtained from Geelong Cement Limited, Australia. Wollastonite (calcium silicate, CaSiO₃) was purchased from Claywork, Melbourne, Australia. All other calcium minerals were purchased from Geological Specimen Supplies, Turramurra, Australia. All CS sources had a particle size distribution of 100% <63μm. Laboratory grade (98% purity) calcium hydroxide (Ca(OH)₂), manufactured by Ajax Chemicals, was also used in the investigation.

The same metakaolin (MK) as used in previous chapters, was also used as the primary aluminosilicate source in this study (Refer to Section 4.1.2 for a full description of the
MK). The oxide compositions of the commercial metakaolin and the CS sources are shown in Table 6.1, which were obtained by X-Ray Fluorescence (XRF) analysis (Section 3.4.1).

Sodium silicate solution was supplied by PQ Australia, Sydney under the brand name of Vitrosol N48 (with 28.7% SiO₂, 8.9% Na₂O and 62.4% H₂O; density 1370kg/m³). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the work. Fine washed sand (100% < 2mm) was used as the aggregate in the samples that were subjected to the compressive strength testing.

6.2.2 Synthesis

Controlled calcium-free geopolymeric binders (Matrices S1, S2 and S3) were prepared by mixing metakaolin with three different sets of alkaline activators prepared at different alkalinity (Ms = SiO₂/Na₂O = 2.0, 1.5 and 1.2). The mass ratios between MK and the alkaline activator used were 0.69, 0.65 and 0.61 for Ms = 2.0, 1.5 and 1.2 respectively. These ratios were selected so as to maintain consistent water and soluble silicate content in all binders.

In preparing the alkaline activators, sodium hydroxide pearl was mixed with the sodium silicate solution to form an alkaline solution with three different molar ratios (Ms = 2.0, 1.5 and 1.2). The hot solution was then cooled overnight to ambient temperature. Matrices were synthesised using a MK/(MK+CS) mass ratio of 0.8 and 0.6. The mass ratio between the dry mix (MK and CS) and the alkaline mix (sodium hydroxide and sodium silicate solution) was identical to those used in the synthesis of controlled binders (Matrices S1, S2 and S3).

MK and CS were mixed thoroughly until a uniform mix, as far as possible, was produced. The alkaline mix was subsequently stirred with the dry mix to form a paste. The paste was mixed for a further 3 minutes to ensure homogeneity. For samples subjected to the compressive strength test, washed sand (with mass ratio = sand/(MK+CS) = 3) was gradually added to the homogeneous paste until a uniform mixture was formed. The paste was then poured into cylindrical moulds (50mm diameter and 100mm length) and allowed to cure in a laboratory convection oven at 40°C for 24h before being extracted from the moulds and hardened at room
temperature (25°C) until the 7 and 28 day compressive strength testing were conducted. All samples were cured at atmospheric pressure and no attempt has been made to control the humidity during curing.

6.2.3 Analysis

6.2.3.1 Dissolution Testing
In order to determine the leachability of Ca, Si and Al from all the raw materials used, concentrated suspensions were prepared with different concentrations (2.5, 5 and 7.5M) of sodium hydroxide. The suspension contained 50g of solid in 100mL alkali solution. Suspensions were mixed for 1 and 24h before centrifuging, filtrating and diluting with 10% conc. hydrochloric acid (HCl) prior to analysing the elemental concentrations of Ca, Si and Al using ICP-OES. The clear liquid obtained after centrifugation was filtered through a 0.2μm Minisart® membrane filter from Sartorius AG Germany to further remove the suspended solid. The conditions used for the dissolution testing should be similar to those used in normal synthesis. However, due to the complexity of the reactions when soluble alkaline silicate was added to activate metakaolin and/or CS, no soluble silicate was added to the current dissolution experiments. The NaOH concentration of 2M, 5M and 7.5M used in the leaching experiment closely resembled the alkalinity in the synthesis of geopolymer matrices at Ms = 2.0, 1.5 and 1.2 respectively.

6.2.3.2 Compressive Strength Testing
Compressive strength testing was performed as per Australian Standard (AS1012.9-1999) using the average of three 50mm diameter cylinders with a 1:2 diameter to length ratio. All samples were tested at 7 and 28 days. An ELE International Auto Test Compression Machine was used. The top face of the specimen was cut parallel to the bottom face by using a diamond saw prior to the compressive strength testing. The top surface of the sample was capped with fast setting Boral Dental Plaster to ensure the diameter and length ratio remained at 1:2. The plaster was then left to dry at room temperature and atmospheric pressure for at least 3h, prior to testing for compressive strength.
6.2.3.3 X-ray Diffraction (XRD)

X-ray diffractograms were recorded on a PHILIPS PW1800 machine using a Cu Kα anticathode and a scanning rate of 2°/min from 5 to 70° 2-theta to give the structural information of each sample. Identification of various crystalline phases was achieved by comparing the diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data. The specimens were prepared by mechanical grinding using a ring mill. It should be noted that the washed sand was not added to samples subjected to the XRD analysis.

6.2.3.4 Scanning Electron Microscopy (SEM)

A Philips XL30 scanning electron microscope, operated at 20keV was used in analysing the surface morphology of the specimen. EDS (Energy Dispersive Spectroscopy) was used to analyse the elemental composition of the surface of a specimen. A DYNAVAC sputter coater was used in coating the specimen with carbon. Elemental analysis was conducted randomly across the area of interest.

6.3 Results and Discussion

6.3.1 Characteristics of Calcium Silicate Materials (CS)

Two processed materials (GGBFS and cement) and five natural calcium silicate minerals were used in this study. These seven materials cover a range of elemental compositions, mineralogy and crystal structure.

As shown in Table 6.1, the CaO content varies from 64.7 wt.% in cement to 15.4 wt.% in anorthite calcium plagioclase. The SiO₂ content varies from 50.5 wt.% in wollastonite to 20.45 wt.% in cement and likewise, the Al₂O₃ content varies from 31.0 wt.% in anorthite calcium plagioclase to 0.25 wt.% in wollastonite. Tremolite and hornblende contain more than 10 wt.% MgO with hornblende being the only calcium silicate material that contains more than 10 wt.% of Fe₂O₃. Hornblende and anorthite calcium plagioclase are the only two materials that contain some alkali (< 2wt.%), however the concentrations are still low in comparison to the amount of sodium added to the system as the alkaline activator. Therefore, it is assumed that the alkaline present in the resultant products originates from the alkaline activator.
GGBFS is essentially an amorphous calcium silicate. According to x-ray diffraction (XRD) (Figure 6.1), gypsum is the only major crystalline phase found in GGBFS. A detailed description of GGBFS can be found in Section 4.1.3. Cement contains several crystalline and semi-crystalline phases in its composition, which includes various forms of calcium silicate.

The five natural silicate minerals used in the study cover a number of crystal structures in the silicate class of minerals, as indicated in Table 6.2. Wollastonite, hornblende and tremolite are all inosilicates, with wollastonite belonging to the single chain group and, hornblende and tremolite belonging to the double chain group. Prehnite is a phyllosilicate, which has a sheet-like structure. The sheets of prehnite are typically interconnected via layers of cations. These cation layers are weakly bonded and often have water molecules or other neutral molecules trapped between the sheets. Subsequently, prehnite has a much lower hardness than the other silicate minerals (Table 6.2). Anorthite calcium plagioclase is a framework silicate (tectosilicate) belonging to the feldspar group. It is known that there is much variation within the tectosilicate subclass. The aluminium ion in the tectosilicate can easily substitute for up to 50% of the silicon ion in the tetrahedra. In other subclasses this substitution occurs to a more limited extent, but in the tectosilicates it is a major basis of varying structures. While the tetrahedron is nearly the same with an aluminium at its centre, the charge is now a negative five (-5) instead of the normal negative four (-4). Since the charge in a crystal must be balanced, additional cations are needed in the structure and subsequently, there is much variation within this subclass.

It is thought that the mineralogy of the calcium sources will have a significant impact on their extent of dissolution in an alkaline medium, and consequently, their respective reactivities. The interrelationship between the mineralogy and reactivity of different CS sources has a significant influence on how each of them will participate in geopolymerisation. It is anticipated that the physical properties of the resultant products are dependent on the nature of formed phases and their interaction with the unreacted solids.
6.3.2 Extent of Dissolution of Calcium Silicate Materials in an Alkaline Medium

Although there is no universally accepted mechanistic view of geopolymerisation, it is commonly acknowledged that the dissolution of silicon and aluminium governs the initial stage of geopolymerisation (Krivenko, 1994; van Jaarsveld, 2000; Xu and van Deventer, 2000; Xu et al., 2001). The formation of geopolymeric gel depends on the availability of dissociated silicate ‘OSi(OH)₃ and aluminate Al(OH)₄’ monomers in the alkaline medium, which is further dependent on the extent of dissolution of these two species from the original aluminosilicate source (Xu and van Deventer, 2000). In the presence of soluble calcium species, the reactions will become more complex, in which case (1) calcium could precipitate as calcium hydroxide, that will lower the concentration of OH⁻, and the extent of dissolution of silicon and aluminium is known to be dependent on the [OH⁻] and/or (2) calcium could interfere with the formation of the alkaline-geopolymeric gel by reacting with the silicate and aluminate monomers available as shown in the previous chapters. The interaction therefore between calcium, silicon and aluminium species in alkaline medium is expected to have a significant impact on the nature of the resultant product.

Tables 6.3 and 6.4 give the extent of dissolution of MK and all seven calcium silicate sources used in terms of concentration of Si, Al and Ca after 1h and 24h of contact between the solid and alkaline solution. The dissolution testing results show that, in general, the concentration of Si is higher than Al for each of the calcium silicate materials at any given condition, however the converse is observed for MK. Xu and van Deventer (2000) observed the same trend for sixteen different aluminosilicate minerals. The different behaviour of MK could be partly due to the higher content of Al in MK (Table 6.1). Another reason could be the calcination process, which allows aluminate to be detached from the MK surface more rapidly than from other minerals. It is believed that it is the ability of MK to supply dissociated aluminate monomers rapidly during the initial dissolution stage that renders MK one of the most effective raw materials to form geopolymers.

Xu and van Deventer (2000) found that minerals with a framework structure possess a higher extent of dissolution of both Si and Al than di-, ortho-, ring, chain and sheet structures in NaOH solutions. The same trend is noted here, as anorthite calcium
plagioclase (ANO) (framework structure) has a slightly higher extent of dissolution of both Si and Al than prehnite (sheet structure) and a much higher extent of dissolution than any other minerals tested after 24h (Table 6.4). The same trend is observed at the end of 1h (Table 6.3), except that prehnite has a slightly higher extent of dissolution of Si and Al than ANO when 2M or 5M NaOH was used instead. Amongst the three ring silicates used in the study, the single chain wollastonite has a consistently lower extent of dissolution than the other two double chain silicates, i.e. hornblende and tremolite. Although there is a higher percentage of dissolved calcium present in the alkaline medium than in the previous study by Xu and van Deventer (2000), the effects of the mineralogy of silicate minerals on the extent of dissolution of Al and Si are similar.

Xu and van Deventer (2000) suggested that Si and Al appear to have synchro-dissolution behaviour in alkaline solution, which means that Si and Al could dissolve from the mineral surface in some linked form. Table 6.5 shows that the correlation coefficients between the extent of dissolution of Si and Al after 24h vary from 0.91 to 1.0 depending on the concentration of sodium hydroxide. This is in agreement with the findings from Xu and van Deventer (2000). However the correlation between the extent of dissolution of Si and Al at the end of 1h is poor at a higher alkalinity. The significant difference between the correlation coefficients at the end of 1h and 24h in Table 6.5 indicates that after 1h of solid/liquid contact, the system has not reached equilibrium. It is thought that a number of reactions are taking place simultaneously, which include, (1) dissolution from the original source minerals, (2) polymerisation between soluble silicate and aluminate species, and (3) other possible precipitation involving calcium, silicon and aluminium.

The correlation coefficients between the CaO, SiO₂ and Al₂O₃ content in all CS sources and solution phases after 1h and 24h of leaching are shown in Table 6.6. Although a linear regression correlation may not be appropriate in analysing the data, it does indeed provide some general insight into the relative reactivity of each species. Table 6.6 shows that the correlations between Al₂O₃ in the raw materials and solution phase are significantly higher than for CaO and SiO₂ at all alkalinities. The close relationship between aluminate in the solution and the Al₂O₃ content in the raw minerals is likely to be caused by the low reactivity of aluminate with other species in
the alkaline medium in comparison to the dissolved calcium and silicates species. It is suggested that the reactions between silicate and calcium, or precipitation of calcium hydroxide or other types of silicates will take place in preference to reactions between aluminate and other species.

The dissolution results in Tables 6.3 and 6.4 do not show any clear relationship between the mineralogy of calcium silicate sources and the extent of dissolution of calcium. Also, there is no clear correlation between the concentration of calcium and the concentrations of silicon and aluminium at any given condition. As suggested earlier, in the absence of dissolved calcium, dissociated silicate and aluminate monomers will react together to form a geopolymer gel in an alkaline environment. Dissolved calcium may interfere with the polymerisation between silicate and aluminate, and more importantly, calcium could precipitate as calcium hydroxide, which will subsequently lower the concentration of OH⁻ ions. As the dissolution of different materials is dependent on [OH⁻], the changes in [OH⁻] could affect the dissolution rate of the different species from the surfaces of the different materials. Subsequently, the decrease in alkalinity due to the presence of dissolved calcium in reacting with hydroxide ions could further inhibit the geopolymerisation process.

6.3.3 Compressive Strength of MK-CS Binders
The results from the compressive strength testing conducted on the different resultant products synthesised using different CS sources and alkaline conditions are summarised in Table 6.7. The compressive strength of matrices prepared with ANO and TRM using Ms = 2.0 are not shown because these matrices failed to set within three days of curing at 40°C.

It is found that the compressive strength of the binders synthesised from moderate additions of cement and GGBFS were higher than all other binders synthesised from natural calcium silicate minerals. Although the elemental compositions of the different CS sources are similar (Table 6.1), the semi-crystalline/amorphous phase present in the processed materials (i.e. GGBFS and cement) has made them more reactive in the alkaline activation as shown later in this chapter.
Despite the higher strength achieved with the addition of processed CS, the difference between the compressive strength attained with different CS decreases with increasing concentration of NaOH used. As a general trend, the compressive strength of the matrices containing natural CS was increased substantially with increasing NaOH. However, the opposite trend was noted in binders containing GGBFS. Furthermore, the compressive strength of the binder containing cement was not affected by the use of different concentrations of NaOH to the same degree as the other CS sources.

The compressive strengths of the matrices containing natural CS were increased substantially with increasing NaOH used in activation. From the dissolution results (Tables 6.3 and 6.4), it has been shown that the extent of dissolution of Si, Al and Ca from the natural CS is dependent on the concentration of NaOH used. However, the dependence of dissolution of the natural minerals on alkalinity does not completely explain the strong dependence of compressive strength on alkalinity. Instead it is possible that the increased strength is merely determined by the enhanced activation of the MK.

For all CS sources except GGBFS, the optimum compressive strength of the binders was achieved using an alkaline activator with Ms = 1.5. From Table 6.7, the compressive strength of the binder (Matrix S2) synthesised using 100% MK and Ms = 1.5 is nearly double the one using Ms = 1.2 (Matrix S3) or 2.0 (Matrix S1). From Tables 6.3 and 6.4, the extent of dissolution of Si and Al from MK using NaOH = 5M is clearly shown to be the highest. It is expected that geopolymerisation will take place in an alkaline medium that gives the greatest extents of dissolution of both Si and Al from the source material. Moreover, comparing the difference between the extent of dissolution of silicon and aluminium from source materials in Tables 6.3 and 6.4, the difference between the extent of dissolution of Si and Al using NaOH = 5M and 7.5M after 24h is minimal in comparison to the result obtained after 1h of initial contact between the MK and the sodium hydroxide solution. It is suggested that in order to achieve a high degree of geopolymerisation, it is essential to have an aluminosilicate source material, which can have its aluminium and silicon species readily dissolved at the initial stage of contact between the solid and alkaline activator.
This enhanced alkaline activation of MK is postulated to be the main reason for the higher compressive strength attained in binders with the addition of natural CS with increasing NaOH used. In other words, in a highly alkaline environment, the geopolymeric gel resulting from the alkaline activation of MK is thought to be the major phase responsible for the binding property. Hence, the mechanical properties of the resultant products are dependent on the geopolymeric gel formed regardless of the type of CS used.

At a low alkalinity (Ms = 2.0), the MK is not able to produce enough aluminate and silicate species to promote the formation of geopolymer, thus the compressive strength of the resultant binder is lower as demonstrated in Chapters 4 and 5. However, the moderate additions of cement will improve the mechanical property of such binder similarly to the addition of GGBFS as shown in Chapters 4 and 5. It is postulated that the alkaline activation of the cement will lead to the formation of some calcium silicate phases, similar to GGBFS, that may assist the geopolymeric gel in contributing to the binding property of the resultant matrix as discussed later in the present chapter.

6.3.4 Characterisation of MK-CS Binders using XRD

Figure 6.1 shows XRD diffractograms of binders resulting from the alkaline activation of metakaolin with 20 wt.% of GGBFS using three different alkaline conditions (Matrices A1, A3 and A5) at 28 days. XRD diffractograms of raw MK and GGBFS used in the synthesis are also shown. It was found that gypsum, which is the only crystalline phase present in GGBFS, was totally dissolved as a result of the alkaline activation. No crystalline phase of significant quantity was detected from the XRD analysis and the resultant binders remained highly amorphous to XRD. Due to the high amorphous content of the resultant binder, it is not possible to identify the different amorphous and semi-crystalline phases present.

Figure 6.2 shows the XRD diffractograms of the binder synthesised from the alkaline activation of metakaolin with 20 wt.% of cement at 28 days using Ms = 1.2 (Matrix B5) and 2.0 (Matrix B1) as well as the raw MK and cement used. Similar to the XRD diffractograms of binders containing GGBFS (Figure 6.1), there is no new crystalline peak detected in the resultant binder synthesised at all alkaline conditions used. This
also indicates that crystalline calcium silicate hydrate (CSH) and crystalline calcium hydroxide, which are the common phases resulting from the hydration of cement, are not the major products forming in the alkaline activated system.

The XRD diffractogram of the raw cement (CEM) (Figure 6.2) shows that cement contains several distinct peaks associated with a number of crystalline calcium silicate phases. Since there is no significant crystalline phase detected in the resultant binder after the alkaline activation, it indicates that there is no significant amount of undissolved cement particles retained in the resultant product. It is suggested that most of the crystalline calcium silicate phases present in the raw cement have been dissolved and reacted in the alkaline solution to become part of the amorphous structure.

Figure 6.3 shows the XRD diffractogram of the binder resulting from the alkaline activation of metakaolin with 20 wt.% of wollastonite (Matrices C1 and C5) using Ms = 2.0 and 1.2 respectively. Unlike either cement or GGBFS, there are still significant amounts of undissolved wollastonite present after the alkaline activation at all alkaline conditions used. This indicates that not all of the calcium and silicon from wollastonite has been dissolved. In fact this is a common feature found in all matrices synthesised from natural minerals. The XRD diffractograms of binders synthesised with ANO, PRH, TRM and HRN are presented in Figures 6.4 to 6.7. In other words, despite the increased dissolution of natural minerals at high alkalinity (Tables 6.3 and 6.4), natural calcium silicate minerals are not as reactive as the processed materials in participating in the reactions in the alkaline activated system.

From Figures 6.1 to 6.7, it is found that a very small “hump” forms at around 27-35°, with the centre being at ~25-29° 2-theta in all binders synthesised; the same hump is also observed when natural minerals were used. It was suggested by van Jaarsveld (2000) that this “hump” was an indication of the presence of the amorphous alkaline aluminosilicate (geopolymer) in the resultant structure as discussed in Chapter 4. It is important to note however, that other materials, including CSH and MK, can exhibit a hump in this region as well.
In order to give a better representation of how the addition of different calcium sources affects the characteristics of the resultant geopolymeric binder, an X-ray diffractogram was plotted as the difference between the diffractogram of the resultant binder at 28 days after the alkaline activation using Ms = 1.2 and the raw materials used before activation. It was calculated by subtracting the “diffractogram before activation” from the “diffractogram after activation” and these “difference” diffractograms will highlight the phases created and destroyed during the alkaline activation.

Figure 6.8 shows that all “difference” diffractograms have similar characteristics regardless of the mineralogy of the calcium silicate used. There is huge sharp decrease in intensity in all of the “difference” diffractogram starting at about 26.4 to 26.7° 2-theta, followed by a gradual increase in the intensity until it reaches a maximum at around 29.5° 2-theta and then another decrease until it reaches 35° 2-theta. The sharp reductions in various places along the XRD spectra are associated with the reaction of different crystalline phases present in the original source materials. This suggests that all calcium silicate sources dissolved to some extent, however, the extent of reaction is dependent on the mineralogy of the calcium sources. Figure 6.9 highlights the “difference” XRD diffractograms of Figure 6.8 in the region between 25 to 29° 2-theta.

The “difference” diffractogram of the standard Ca(OH)₂ binder synthesised in the same way as the other CS sources as described earlier in Section 6.2.2, is also shown in Figures 6.8 and 6.9. It is found that the diffractogram has similar characteristics to the other binders using the CS. This indicates that all calcium species that dissolved from the original calcium silicate source would behave in a similar way as if calcium hydroxide is added to the system.

A standard geopolymeric (STD) binder (Matrix S3) without the addition of any calcium silicate is also plotted in Figures 6.8 and 6.9. This plot shows that the XRD diffractograms of the binders containing calcium silicate have the same characteristics as the geopolymeric binder synthesised without any addition of CS. This means that the addition of the calcium silicate to an alkaline activated MK system does not play a role in changing the structure of the geopolymers synthesised. The sodium based
geopolymer remains as the dominant phase forming in all matrices studied in this investigation despite the addition of various types of calcium silicate minerals.

6.3.5 Microstructure of the MK-CS Binders
Figures 6.10 and 6.11 show the microstructure of a geopolymeric product with a moderate addition (20 wt.%) of CEM synthesised from Ms = 2.0 and 1.2 respectively. Similar to the microstructure of the MK-GGBFS (Matrix A1) binder synthesised with an identical amount of calcium silicate source added (Figure 5.1), two separate phases, namely geopolymeric and calcium silicate hydrate gels were formed simultaneously in the MK-CEM binder (Matrix B1). Further EDS analysis on the two phases, confirms the formation of CSH gel within a geopolymeric gel. The average concentration of calcium in the geopolymeric gel is less than 2mol%. The XRD analysis as shown earlier revealed that there is no new crystalline product formed as the result of the alkaline activation of MK in the presence of CEM. The semicrystalline to crystalline CSH phases commonly formed as a result of the hydration of CEM, are not products formed in an alkaline activated system. Subsequently, the CSH found forming within the geopolymeric gel in the current MK-CEM system is suggested to be an amorphous product with higher aluminium content, and is different from the one commonly formed in ordinary Portland cement.

In contrast to the large amount of calcium-containing species found scattered in the MK-GGBFS binder synthesised at a highly alkaline system (Ms = 1.2) as discussed in Section 5.3.2, the coexistence of both geopolymeric and CSH gels remains as the dominant feature found in MK-CEM binder (Matrix B5) synthesised in such condition. The growth of CSH in a geopolymeric gel upon the addition of CEM is found to be independent of the alkaline condition used within the range studied. This is likely to be the result of the larger extent of dissolution of calcium and silicate from CEM in comparison to GGBFS, as demonstrated in the dissolution testing (Tables 6.3 and 6.4). Subsequently, despite the rapid crystallisation of calcium hydroxide in a highly alkaline environment, the larger extent of dissolution of calcium from CEM, will provide enough soluble calcium and silicate species in alkaline environment to initiate the formation of CSH gel in the geopolymeric gel. Thus, the coexistence of both gels remains the dominant micro-feature of the alkaline activated MK-CEM system. Moreover, given that the size of the CSH gel formed in the geopolymeric gel is
relatively large (~60 to 100μm in diameter), the binding property of the MK-CEM system will not be based on the geopolymeric gel alone. Rather, similar to the MK-GGBFS binder synthesised at low alkalinity, the improved compressive strength achieved in the system is the result of the coexistence of both CSH and geopolymeric gels simultaneously.

Figures 6.12 to 6.16 show the microstructures of the geopolymeric product with 20 wt.% of different crystalline calcium silicate (CS) source added to the system synthesised at various alkaline conditions. These micrographs illustrate a prominent feature found in such systems, i.e. despite a small quantity of calcium precipitates being observed, in general, a large amount of unreacted raw crystalline CS particles was found scattered in the geopolymeric product. The SEM results are in agreement with the XRD results presented in Section 6.3.4. The reactivity of crystalline CS minerals is much lower than that of processed CS sources (i.e. GGBFS or CEM) in the alkaline activated system. Subsequently, a significant amount of raw crystalline CS particles were retained in the resultant geopolymeric product.

A clear coexistence between the geopolymeric and CSH phases could not be found in systems containing crystalline CS material in all alkaline conditions studied. Increasing the amount of crystalline CS being added to the system would only result in binders with an increasing concentration of unreacted raw CS particles situated in the geopolymeric gel. EDS analysis conducted on the geopolymeric gel formed in these systems, showed that the average concentration of calcium is less than 1mol.%. This indicates that the possible calcium movement from crystalline calcium silicate source to participate in geopolymerisation is more restricted than from processed calcium silicate source. The failure to form CSH within the geopolymeric gel is likely to be the result of the lack of dissolved calcium species present in the system. Subsequently, the geopolymeric gel is also confirmed to be the major constituent, which contributes to the binding property of such binders. Crystalline calcium silicate sources are merely acting as an aggregate or filler in enhancing the physical structure of the resultant matrix.
6.3.6 Mechanistic Considerations

Given that most of the crystalline phases in GGBFS and cement have reacted during the alkaline activation, it is anticipated that dissolved calcium species would take part in formation of new phases in the resultant binder. In fact, this has already been demonstrated in the MK-GGBFS system as presented in Chapters 4 and 5. The current chapter has confirmed the results with new evidence from the MK-CEM system. Furthermore, based on the significant increase in compressive strength in matrices containing moderate amounts of either GGBFS or cement (Table 6.7) at low alkalinity (Ms = 2.0), it has verified that the new predominately amorphous calcium phase will play a significant structurally determining role in the resultant binder.

Alonso and Palomo (2001a, b) found that in the presence of calcium hydroxide, the alkaline activation of MK would lead to the formation of both geopolymeric and CSH gels. The results presented in Chapters 4 and 5, also confirmed that both geopolymeric gel and CSH gel are formed simultaneously in an alkaline activated MK system in the presence of GGBFS. It is proposed that in an alkaline activated system at low alkalinity (Ms = 2.0), the presence of dissolved calcium originating from various CS sources will behave similarly, whereby both geopolymeric gel and amorphous CSH gel are formed in the same system.

As shown in Table 6.7, the addition of moderate quantities (CS/(MK+CS)=0.2) of processed calcium silicate (GGBFS and cement) will improve the compressive strength of matrices significantly. XRD analysis (Figures 6.1 and 6.2) reveals that most of the original crystalline and semicrystalline phases present in GGBFS and cement have reacted in the alkaline medium. Therefore it is suggested that higher compressive strength of the matrices could be achieved if the dissolution rate of the original calcium sources is high. It is the ability of the processed CS sources to readily dissolve calcium into the alkaline medium that makes them reactive to form CSH gel in conjunction with the geopolymeric gel, and gives rise to the improved compressive strength of the resultant matrices. This finding is in agreement with Glukhovsky’s hypothesis (Glukhovsky, 1994). Moreover, the significantly better compressive strength achieved for the MK-CEM system in comparison to the MK-GGBFS system at high alkalinity (Ms = 1.5 and 1.2) is suggested to be the result of its
ability to form both CSH and geopolymeric gels in the structure in a highly alkaline environment, which the MK-GGBFS system failed to do.

Dissolved calcium species originating from natural CS sources will behave similarly to calcium originating from processed CS. However, crystalline CS minerals, due to their much slower dissolution rate in an alkaline environment, as is evident from the high percentage of undissolved particles retained in the resultant product as shown in XRD and SEM results, are unable to provide sufficient dissolved calcium species to form adequate amounts of amorphous calcium silicate gels in the system. Thus, the binding property of such a binder is based mainly on the geopolymeric gel formed from the alkaline activation of MK.

At low alkalinity, the extent of dissolution of Si and Al from MK is too low to produce a sufficient amount of dissolved silicate and aluminate monomers to form a highly ordered geopolymeric gel. The lack of a highly ordered structure in the geopolymeric gel will result in a binder with poor strength.

At high alkalinity, the dissolution of Si and Al from MK is sufficient so that an ordered aluminosilicate geopolymeric gel forms. Subsequently, the compressive strength of the binders containing natural CS sources is much higher than those synthesised using low alkalinity despite the fact there is still insufficient dissolved calcium available to form a CSH gel (Table 6.7). The relatively small difference in the compressive strength between the binders containing different types of CS sources (Table 6.7) also suggests that the geopolymeric gel is the dominant phase forming in a highly alkaline system. The presence therefore of dissolved calcium species will only play a minor role in affecting the main structure of the resultant product.

It is possible that a significant amount of the undissolved calcium silicate minerals will act as reinforcement in the resultant matrices. Consequently, the physical and surface properties of the minerals will have a major impact on how they will reinforce the resultant matrices, hence there is a small observable difference in compressive strengths between the matrices synthesised using different natural calcium silicate sources.
6.4 Conclusion

The results presented in this chapter show that the effects of different calcium silicate sources on geopolymerisation are dependent on the mineralogy of the calcium silicate sources as well as the alkalinity of the alkaline activator.

The dissolution of calcium from processed calcium silicate sources at low alkalinity forms CSH gel in conjunction with the geopolymeric gel in the same system, which enhances the compressive strength. Less calcium dissolves from the natural calcium silicate minerals, so that there is insufficient CSH gel in the binder, hence giving weaker matrices. This result also suggests that the coexistence of both geopolymeric gel and CSH gel gives rise to the satisfactory mechanical properties of the matrices synthesised at low alkalinitities.

Geopolymeric gel appears to be the dominant product formed at high alkalinitities. Calcium plays a lesser role in affecting the nature of the end product, thus the extent of dissolution of calcium species from the different calcium silicate sources will not have a major impact on the resultant strength of the matrices. Subsequently, the compressive strengths of the matrices synthesised at high alkalinity were found to be similar regardless of the types of calcium silicate minerals used.

The thesis has so far studied the role of various calcium silicate sources in geopolymerisation, in which there is no significant amount of "foreign" anion, other than hydroxide and silicate ions in the system. The next two chapters will investigate the effect of calcium sources, containing "foreign" anions, such as sulphate (gypsum plaster) and carbonate (calcite), on geopolymerisation.
<table>
<thead>
<tr>
<th>Material</th>
<th>Symbol</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metakaolin</td>
<td>MK</td>
<td>0.10</td>
<td>54.8</td>
<td>40.42</td>
<td>0.76</td>
<td>0.41</td>
<td>2.72</td>
<td>0.07</td>
</tr>
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<td>Ground granulated blast furnace slag</td>
<td>GGBFS</td>
<td>43.0</td>
<td>34.4</td>
<td>14.1</td>
<td>0.11</td>
<td>6.3</td>
<td>0.33</td>
<td>0.3</td>
</tr>
<tr>
<td>Cement</td>
<td>CEM</td>
<td>64.7</td>
<td>20.45</td>
<td>4.58</td>
<td>3.72</td>
<td>1.67</td>
<td>0.39</td>
<td>0.67</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>WOL</td>
<td>47.5</td>
<td>50.5</td>
<td>0.25</td>
<td>0.2</td>
<td>0.25</td>
<td>0.33</td>
<td>0.3</td>
</tr>
<tr>
<td>Anorthite Calcium Plagioclase</td>
<td>ANO</td>
<td>15.43</td>
<td>47.38</td>
<td>31.02</td>
<td>0.84</td>
<td>1.42</td>
<td>0.57</td>
<td>1.26</td>
</tr>
<tr>
<td>Hornblende</td>
<td>HRN</td>
<td>21.39</td>
<td>50.4</td>
<td>0.95</td>
<td>11.96</td>
<td>11.52</td>
<td>0.04</td>
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</tr>
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<td>Prehnite</td>
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<td>42.23</td>
<td>22.73</td>
<td>1.72</td>
<td>0.1</td>
<td>0.01</td>
<td>0.09</td>
</tr>
<tr>
<td>Tremolite</td>
<td>TRM</td>
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<td>44.53</td>
<td>1.68</td>
<td>2.03</td>
<td>18.74</td>
<td>0.09</td>
<td>0.17</td>
</tr>
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Table 6.2: Physical properties of calcium silicate source (CS) materials. (Crystallinity: A = amorphous, B = semi-crystalline and C = crystalline)

<table>
<thead>
<tr>
<th>Material</th>
<th>CS</th>
<th>Crystallinity</th>
<th>Mineral Group</th>
<th>Silicate Group</th>
<th>Crystal System</th>
<th>Ideal Stoichiometry</th>
<th>Hardness (Mohs)(^1)</th>
<th>Density (g/cm(^3))(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground granulated blast furnace slag Cement</td>
<td>GGBFS</td>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wollastonite</td>
<td>CEM</td>
<td>B,C</td>
<td>C</td>
<td>Silicate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anorthite calcium plagioclase Hornblende</td>
<td>ANO</td>
<td>C</td>
<td>C</td>
<td>Silicate</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Prehnite Tremolite</td>
<td>PRH</td>
<td>C</td>
<td>C</td>
<td>Silicate</td>
<td></td>
<td></td>
<td></td>
<td></td>
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\(^1\) CRC Handbook of Chemistry and Physics, 2000
Table 6.3: The extent of dissolution of Ca, Si and Al from various source materials using NaOH solution. Dissolution time is 1 hour.

<table>
<thead>
<tr>
<th>Material</th>
<th>2M NaOH</th>
<th>5M NaOH</th>
<th>7.5M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca (ppm)</td>
<td>Si (ppm)</td>
<td>Al (ppm)</td>
</tr>
<tr>
<td>MK</td>
<td>58</td>
<td>1320</td>
<td>1723</td>
</tr>
<tr>
<td>GGBFS</td>
<td>53</td>
<td>379</td>
<td>159</td>
</tr>
<tr>
<td>CEM</td>
<td>96</td>
<td>89</td>
<td>3</td>
</tr>
<tr>
<td>WOL</td>
<td>46</td>
<td>41</td>
<td>1</td>
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<tr>
<td>ANO</td>
<td>43</td>
<td>486</td>
<td>353</td>
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<tr>
<td>HRN</td>
<td>125</td>
<td>84</td>
<td>9</td>
</tr>
<tr>
<td>PRH</td>
<td>73</td>
<td>511</td>
<td>382</td>
</tr>
<tr>
<td>TRM</td>
<td>96</td>
<td>89</td>
<td>5</td>
</tr>
</tbody>
</table>
Table 6.4: The extent of dissolution of Ca, Si and Al from various source materials using NaOH solution. Dissolution time is 24 hours.

<table>
<thead>
<tr>
<th>Material</th>
<th>2M NaOH</th>
<th>5M NaOH</th>
<th>7.5M NaOH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca (ppm)</td>
<td>Si (ppm)</td>
<td>Al (ppm)</td>
</tr>
<tr>
<td>MK</td>
<td>24</td>
<td>1015</td>
<td>1560</td>
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<tr>
<td>GGBFS</td>
<td>16</td>
<td>228</td>
<td>210</td>
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<tr>
<td>CEM</td>
<td>58</td>
<td>82</td>
<td>8.2</td>
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<tr>
<td>WOL</td>
<td>28</td>
<td>125</td>
<td>21</td>
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<tr>
<td>ANO</td>
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<td>927</td>
<td>1625</td>
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<tr>
<td>PRH</td>
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<td>863</td>
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<tr>
<td>TRM</td>
<td>250</td>
<td>144</td>
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Table 6.5: Correlation coefficients for a linear regression analysis between the concentrations of Si and Al in the solution phase after 1h and 24h of dissolution.

<table>
<thead>
<tr>
<th>[NaOH]</th>
<th>1h</th>
<th>24h</th>
</tr>
</thead>
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<tr>
<td>2M</td>
<td>0.97</td>
<td>1.00</td>
</tr>
<tr>
<td>5M</td>
<td>0.35</td>
<td>0.96</td>
</tr>
<tr>
<td>7.5M</td>
<td>0.24</td>
<td>0.91</td>
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</tbody>
</table>

Table 6.6: Correlation coefficients for a linear regression analysis between the CaO, SiO₂ and Al₂O₃ content in the raw material and in solution after 1h and 24h of dissolution testing.

<table>
<thead>
<tr>
<th>[NaOH]</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1h</td>
<td>24h</td>
<td>1h</td>
</tr>
<tr>
<td>2M</td>
<td>-0.07</td>
<td>-0.63</td>
<td>0.18</td>
</tr>
<tr>
<td>5M</td>
<td>-0.29</td>
<td>0.38</td>
<td>-0.63</td>
</tr>
<tr>
<td>7.5M</td>
<td>0.93</td>
<td>0.29</td>
<td>-0.32</td>
</tr>
</tbody>
</table>
Table 6.7: Compressive strengths of resultant matrices synthesised using different Ms.

<table>
<thead>
<tr>
<th>Calcium (CS)</th>
<th>MK / (MK + CS)</th>
<th>Ms = 2.0</th>
<th>Ms = 1.5</th>
<th>Ms = 1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Matrix 7-day (MPa)</td>
<td>28-day (MPa)</td>
<td>Matrix 7-day (MPa)</td>
<td>28-day (MPa)</td>
</tr>
<tr>
<td>-- 8</td>
<td>1 S1</td>
<td>34.6</td>
<td>35.2</td>
<td>S2</td>
</tr>
<tr>
<td>GGBFS 0.8</td>
<td>A1</td>
<td>47.1</td>
<td>54.2</td>
<td>A3</td>
</tr>
<tr>
<td>GGBFS 0.6</td>
<td>A2</td>
<td>41.5</td>
<td>52.7</td>
<td>A4</td>
</tr>
<tr>
<td>CEM 0.8</td>
<td>B1</td>
<td>47.5</td>
<td>53.5</td>
<td>B3</td>
</tr>
<tr>
<td>CEM 0.6</td>
<td>B2</td>
<td>31.2</td>
<td>28.1</td>
<td>B4</td>
</tr>
<tr>
<td>WOL 0.8</td>
<td>C1</td>
<td>&lt;5.0</td>
<td>18.8</td>
<td>C3</td>
</tr>
<tr>
<td>WOL 0.6</td>
<td>C2</td>
<td>&lt;5.0</td>
<td>16.8</td>
<td>C4</td>
</tr>
<tr>
<td>ANO 0.8</td>
<td></td>
<td></td>
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<td>D3</td>
</tr>
<tr>
<td>ANO 0.6</td>
<td></td>
<td></td>
<td></td>
<td>D4</td>
</tr>
<tr>
<td>HRN 0.8</td>
<td>E1</td>
<td>&lt;5.0</td>
<td>8.3</td>
<td>E3</td>
</tr>
<tr>
<td>HRN 0.6</td>
<td>E2</td>
<td>&lt;5.0</td>
<td>5.7</td>
<td>E4</td>
</tr>
<tr>
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<td>F1</td>
<td>6.7</td>
<td>14.3</td>
<td>F3</td>
</tr>
<tr>
<td>PRH 0.6</td>
<td>F2</td>
<td>6.2</td>
<td>11.5</td>
<td>F4</td>
</tr>
<tr>
<td>TRM 0.8</td>
<td></td>
<td></td>
<td></td>
<td>G3</td>
</tr>
<tr>
<td>TRM 0.6</td>
<td></td>
<td></td>
<td></td>
<td>G4</td>
</tr>
</tbody>
</table>

a. MK only
Figure 6.1: X-ray diffractogram of raw MK, raw GGBFS, the sample (20% GGBFS and 80% MK) before alkaline activation (AA), and the resultant binders (Matrices A1, A3 and A5) synthesised using Ms = 2.0, 1.5 and 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and G – Gypsum (JCPDS 33-0311))
Figure 6.2: X-ray diffractogram of raw MK, raw cement, the sample (20% CEM and 80% MK) before alkaline activation (AA), and the resultant binders (Matrices B1 and B5) synthesised using Ms = 2.0 and 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and C – various calcium silicate hydrate phases including Ca$_3$SiO$_5$ (JCPDS 42,551) and CaSiO$_3$ (JCPDS 45,156))
Figure 6.3: X-ray diffractogram of raw MK, raw wollastonite, the sample (20% WOL and 80% MK) before alkaline activation (AA), and the resultant binders (Matrices C1 and C5) using Ms = 2.0 and 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and W – wollastonite (CaSiO₃, JCPDS 27-0080))
Figure 6.4: X-ray diffractogram of raw MK, raw anorthite calcium plagioclase (ANO), the sample (20% ANO and 80% MK) before alkaline activation (AA), and the resultant binders (Matrix D5) using Ms = 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and A – Anorthite calcium plagioclase (CaAlSi$_3$O$_8$, JCPDS 41-1486))
Figure 6.5: X-ray diffractogram of raw MK, raw hornblende (HRN), the sample (20% HRN and 80% MK) before alkaline activation (AA), and the resultant binders (Matrices E1 and E5) using Ms = 2.0 and 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and H – Hornblende (JCPDS 02-0568))
Figure 6.6: X-ray diffractogram of raw MK, raw prehnite (PRH), the sample (20% PRH and 80% MK) before alkaline activation (AA), and the resultant binders (Matrices F1 and F5) using Ms = 2.0 and 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and P – Prehnite (JCPDS 29-0290))
Figure 6.7: X-ray diffractogram of raw MK, raw tremolite (TRM), the sample (20% TRM and 80% MK) before alkaline activation (AA), and the resultant binders (Matrix G5) using Ms = 1.2 at 28 days. (M – Muscovite 3T (JCPDS 07-0042) and T – Tremolite (JCPDS 44-1402))
Figure 6.8: Differences between the x-ray diffractogram of matrices with different CS in the ratio of 80% MK and 20% CS before and after alkaline activation (Ms = 1.2).
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Figure 6.10: Scanning electron micrographs of Matrix B1 (20% Cement, Ms = 2.0) at 28 days. Figure 6.10II shows the magnified view of Figure 6.10I. A – geopolymeric binder with low content of calcium; B – calcium silicate hydrate with a small proportion of aluminium.
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Figure 6.12: Scanning electron micrographs of Matrix C5 (20% Wollastonite, Ms = 1.2) at 28 days. Figure 6.12II shows the magnified view of Figure 6.12I with Area A being a geopolymeric binder with low content of calcium.
Figure 6.13: Scanning electron micrographs of Matrix D5 (20% anorthite calcium plagioclase, Ms = 1.2) at 28 days, which highlights the high concentration of unreacted ANO particle in the structure.
Figure 6.14: Scanning electron micrographs of Matrix E1 (Ms = 2.0) and E5 (Ms = 1.2) using 20% hornblende at 28 days, which highlights the unreacted hornblende particle scattering in the geopolymeric phase (A).
Figure 6.15: Scanning electron micrographs of Matrix F1 (Ms = 2.0) and F5 (Ms = 1.2) using 20% prehnite at 28 days, which highlights the unreacted prehnite particle scattering in the geopolymeric gel (A) and some calcium phases (C) formed around the geopolymeric phase (A).
Figure 6.16: Scanning electron micrographs of Matrix G5 (20% tremolite, Ms = 1.2) at 28 days, which highlights the high concentration of unreacted tremolite particle in the structure.
Chapter 7

Effect of Calcium Sulphate Hemihydrate (CaSO₄·0.5H₂O) on Geopolymerisation

Chapters 4 to 6 have examined the behaviour of different calcium silicate sources during geopolymerisation. However, it is still unclear how the presence of different anionic species originating from calcium sources could possibly interfere or alter the effect that calcium has in the geopolymerisation process. This chapter will therefore focus on the effect sulphate has on the role calcium plays in geopolymerisation.

The addition of a small amount (up to 20% by mass) of commercially available gypsum plaster (containing mainly calcium sulphate hemihydrate (HEM) with detectable amounts of calcite) is found to improve the compressive strength of a metakaolin (MK)-based geopolymeric binder. This indicates that the sulphate ion (in the presence of dissolved calcium species) could have a positive effect on the mechanical property of the resultant geopolymeric products. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) reveals that calcium silicate hydrate and sodium sulphate phases are formed in the geopolymeric gel. Gypsum (calcium sulphate dihydrate), ettringite (calcium aluminosulphate hydrate), and a calcium-based geopolymer phase (amorphous calcium aluminosilicate network) could not be detected in any of the alkaline activated MK-HEM matrices synthesised. The nature of the long-term products of an alkaline activated MK-HEM system is found to be independent of the initial alkalinity of the activator (SiO₂/Na₂O molar ratio of 1.2 to 2.0). It is observed that the alkalinity of the activator affects the initial reaction rates in the system. The presence of sulphate ions in a MK-HEM system could enhance the formation of the more crystalline form of calcium silicate hydrate in a geopolymeric gel.
(The work presented in this chapter is based on the manuscript: C.K. Yip, G.C. Lukey and J.S.J. van Deventer, “The Alkaline Activation of Metakaolin in the Presence of Calcium Sulphate Hemihydrate (CaSO₄·0.5H₂O),” Cement and Concrete Research, Accepted 2004).

7.1 Background

The main constituent of commercial gypsum plaster (plaster of Paris) is calcium sulphate hemihydrate (bassanite), CaSO₄·0.5H₂O. Gypsum plaster sets quickly upon the addition of water due to its natural process of crystallisation. The reaction mechanism for the hydration process has been well studied (Solberg and Hansen, 2001; Chappuis, 1999). It is generally agreed that the mechanism involves the dissolution of the hemihydrate and a crystallisation of the gypsum (CaSO₄·2H₂O), which has a much lower solubility following the reaction as shown in Equation 7.1:

\[
\text{CaSO}_4\cdot0.5\text{H}_2\text{O} + 1.5\text{H}_2\text{O} \rightarrow \text{CaSO}_4\cdot2\text{H}_2\text{O}
\] (7.1)

It is currently common practice to add gypsum to cement clinker in order to delay the setting of ordinary Portland cement (OPC) by the deposition of ettringite (calcium aluminosulphate hydrate, 3CaO·Al₂O₃·3Ca(SO₄)₂·32H₂O) on cement particles (Buchel et al., 2000). The reaction mechanisms that take place during the hydration of OPC in the presence of gypsum have been well studied in the past century (Irassar et al., 2003; Arikian and Sobolev, 2002; Buchel et al., 2000; Gani, 1997; Hand, 1997; Zhang et al., 1996; Xu and Sarkar, 1991; Taylor, 1964). It has been shown that the addition of a small amount of calcium sulphate hemihydrate has a similar retarding action as gypsum, but when the amount of calcium sulphate hemihydrate increases, it can shorten the setting time through the precipitation of blended crystals of gypsum (Taylor, 1964).

Sulphate “attack” is one of the factors that affects the durability of modern concrete (Irassar et al., 2003, 1996; Santhanam et al., 2002; Taylor et al., 2001; Gollop and Taylor, 1995; Malhotra and Mehta, 1996; Taylor, 1964). It is commonly believed that the mechanism of sulphate attack in OPC can be divided into the following processes:
ettringite formation, gypsum formation and salt crystallisation (Irassar et al., 2003, 1996; Santhanam et al., 2002; Taylor et al., 2001; Malhotra and Mehta, 1996; Gollop and Taylor, 1995; Taylor, 1964). These products occupy a greater volume than the original compounds causing expansion, disruption and cracking in the structure (Irassar et al., 2003, 1996; Santhanam et al., 2002; Taylor et al., 2001; Malhotra and Mehta, 1996; Gollop and Taylor, 1995; Taylor, 1964). As outlined in Chapter 2, geopolymers have been proposed as a possible alternative to OPC (van Jaarsveld, 2000; Davidovits, 1991; Davidovits and Davidovics, 1988), but the impact of possible sulphate attack on geopolymerisation has not been studied. The possible formation of gypsum and ettringite, which could disrupt the geopolymeric structure similarly to OPC needs to be investigated.

Previous research has suggested that the calcium cation has a similar role, as sodium and potassium, in the balancing of the negative charge present in the aluminosilicate network (Davidovits, 1999, 1991). However, it has been demonstrated in Chapters 4 to 6, that calcium-based geopolymers are not formed in a low-temperature, mildly alkaline activated system, with calcium hydroxide as the alkaline activator or calcium originating from a calcium silicate source. Instead, it has been found that calcium silicate hydrate (CSH) gel is the dominant phase formed in a lowly alkaline system (molarity of NaOH ≈ 2.5 to 5M), coexisting with an alkali cation based geopolymer that is similar to the one which forms in the absence of a soluble calcium source. However in highly alkaline conditions, CSH gel was not observed to be a phase presented in the system, rather a high concentration of calcium precipitates was found scattered within the geopolymeric gel. The chemical mechanisms responsible for the formation of both geopolymeric and CSH gels simultaneously have been proposed and discussed in Chapters 4 to 6.

The results presented in the thesis have so far been restricted to calcium originating from different calcium hydroxide or calcium silicate sources. The anionic effect of hydroxide and silicate ions in influencing the role of calcium in geopolymerisation cannot be clearly shown in these systems, as hydroxide and silicate are also present in the alkaline activator used.
This chapter will therefore investigate the physical and mechanistic effects of calcium sulphate hemihydrate on geopolymerisation. The current work provides an understanding of how calcium during geopolymerisation in the presence of sulphate ions affects the chemical mechanism and the subsequent mechanical properties of geopolymeric binders. This will provide a fundamental understanding on how possible sulphate “attack” would affect the durability of geopolymeric binders.

7.2 Experimental Procedure

Section 3.2 gives a detailed description of the geopolymer sample synthesis. A description of all analytical techniques used in this chapter can be found in Section 3.4.

7.2.1 Materials

Metakaolin (MK), MetaStar 402, obtained from ECC International was used as the primary aluminosilicate source. General information regarding the alkaline activation of MK can be found in Chapters 2 to 4 of the thesis. The calcium sulphate hemihydrate (HEM), Gyprock Base Coat 100 from CSR Ltd, used in this study is categorised as a plaster-based cement and adhesive. This material is used commercially as a gypsum plaster based setting type cement for joining plasterboard to masonry concrete surfaces.

Pure gypsum (calcium sulphate dihydrate, CaSO$_4$.2H$_2$O) is a white to transparent mineral, but sometimes impurities colour it grey, brown, or pink. When gypsum is heated, it loses about three-quarters of its water to become calcium sulphate hemihydrate (HEM). HEM is soft and can be easily ground to a powder called hemihydrate gypsum plaster or plaster of Paris. If this powder is then mixed with water to form a paste or slurry, it will dry and set hard. The water, previously driven off by heating, will recombine, and the material will revert to the original chemical composition of gypsum as shown in Equation 7.1. When HEM gypsum plaster is in slurry form, it can be poured between two paper layers to make wallboards, used to fill cracks and crevices, or poured into moulds to form decorative products. Gypsum

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therefore makes an ideal building material because it is fire resistant, abundant, economical, versatile, and fairly strong since ancient time (Olson, 2000).

The mineralogical composition of HEM used in this study was determined by XRD (Section 3.4.2). Identification of various crystalline phases was achieved by comparing the diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data. The XRD analysis revealed that HEM contains mainly bassanite (calcium sulphate hemihydrate with JCPDS 41-0224), with a small amount of calcite (calcium carbonate with JCPDS 47-1743), and quartz (silica with JCPDS 46-1045) as shown in Figure 7.1. The oxide compositions of MK and HEM, as determined by fusion analysis, using a Siemens SRS3000 sequential X-ray fluorescence (XRF) are shown in Table 7.1.

The sodium silicate solution used was supplied by PQ Australia, Sydney, under the brand name of Vitrosol N48 (with 28.7% SiO₂, 8.9% Na₂O and 62.4% H₂O; density 1.37g/mL). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the work.

### 7.2.2 Synthesis

Controlled geopolymeric binders (without any addition of HEM) were prepared by mixing metakaolin with alkaline activators prepared at three different conditions: \( M_s = \text{SiO}_2/\text{Na}_2\text{O} \) molar ratio of 2.0, 1.5 and 1.2. The mass ratio between MK and the alkaline activator used was 0.69, 0.65, 0.61 for \( M_s = 2.0, 1.5 \) and 1.2 respectively. These ratios were selected in order to maintain consistent water and soluble silicate content in all binders.

Samples were synthesised using mass ratios of HEM/(MK+HEM) of 0.1, 0.2, 0.6 and 1. The mass ratio between the dry mix (MK and HEM) and the alkaline activator solution (containing sodium hydroxide and sodium silicate) was identical to the ratio used in the synthesis of the controlled binders. Geopolymeric binders were synthesised by uniformly mixing MK and HEM. The alkaline activator solution was subsequently stirred with the dry mix to form a paste. The paste was mixed for a further 3 minutes to ensure homogeneity. The paste was then poured into cylindrical moulds (50mm diameter and 100mm length) and allowed to cure in a laboratory
convection oven at 40°C for 24 h before being extracted from the moulds and hardened at 25°C prior to testing at specified times. All samples were cured at atmospheric pressure and no attempt was made to control the humidity during curing. The MK to alkaline activator mass ratio used was the same as previous binders studied; this enables accurate comparison of results. It should be noted that in contrast to all binders synthesised for the compressive strength testing as discussed previously in Chapters 4 to 6, all binders with HEM were synthesised without the addition of washed sand. This is due to the rapid setting of MK-HEM binders.

7.3 Results and Discussion

7.3.1 Geopolymerisation in the Absence of Calcium Sulphate Hemihydrate

The chemical mechanism for the alkaline activation of an aluminosilicate source using either sodium or potassium hydroxide has been well studied (Xu et al., 2001; Phair et al., 2000; van Jaarsveld, 2000; Xu and van Deventer, 2000). As discussed in Chapter 2, the process of geopolymerisation can be summarised into three steps: dissolution, transportation (orientation) and polycondensation (reprecipitation). It is also commonly acknowledged that in geopolymerisation, the alkaline activator will accelerate the dissolution of silicon and aluminium ions by breaking the Si-O and Al-O bonds in the aluminosilicate source. Subsequently, the polymerisation will take place and geopolymeric (amorphous alkaline aluminosilicate) gel will form. It is therefore anticipated that geopolymerisation will be accelerated in a system that exhibits a greater extent of dissolution of silicon and aluminium.

Using the same methodology as outlined in Section 3.2, a series of geopolymer samples have been formed using different SiO₂/Na₂O molar ratios. Table 7.2 shows that the compressive strength of geopolymeric binders synthesised using metakaolin is dependent on the SiO₂/Na₂O molar ratio of the alkaline activator. Since the concentration of soluble silicate in the alkaline activator was kept at a constant value, the extent of geopolymerisation, and therefore the resultant compressive strength of the binder, is dependent on the molarity of NaOH. However, an optimum molar ratio between SiO₂ and Na₂O does exist that gives rise to the highest compressive strength as shown for binders of Ms = 1.5. It should also be noted that the binders of Ms = 1.2
attained a higher compressive strength than that of Ms = 2.0. The main reason for this behaviour is possibly due to the higher extent of dissolution of silicon and aluminium from metakaolin at the higher alkali concentration (Ms = 1.2).

The results of the dissolution tests conducted on metakaolin (Section 6.2.3.1) are presented in Figure 7.2. It is shown that the extent of dissolution of silicon and aluminium from metakaolin is dependent upon the concentration of sodium hydroxide used during leaching. Figure 7.2 shows that the concentration of silicon and aluminium species in solution increases with alkali concentration for a total leaching period of 24h. However, it is observed from the initial dissolution (after 1h period), that a higher extent of dissolution of both aluminium and silicon occurs for 5M NaOH, rather than for the high alkali concentration of 7.5M.

Although the effect of silicate is not included, these results suggest that the initial rate of dissolution of silicon and aluminium from MK (or any aluminosilicate source) could significantly affect the extent of geopolymerisation that takes place, in addition to the total amount of aluminium and silicon dissolved.

7.3.2 Alkaline Activation of Calcium Sulphate Hemihydrate

It is well known that calcium sulphate dihydrate (gypsum) is the main product formed by the hydration of calcium sulphate hemihydrate (Equation 7.1). However, XRD analysis shows clearly that gypsum (JCPDS 36-0432 with characteristic peaks at d-spacing 3.06, 4.28 and 7.59Å) is not formed by the alkaline activation of calcium sulphate hemihydrate using alkali activator with Ms = 1.2 (Figures 7.1 and 7.3).

The XRD analysis also reveals that there is still a significant amount of unreacted quartz and calcite present after 2 days of reaction, however, it appears that the bassanite (calcium sulphate hemihydrate) present in the raw material has reacted with sodium hydroxide and sodium silicate to form new phases, including: calcium silicate hydrate (Ca$_{1.5}$SiO$_{3.5}$xH$_{2}$O with JCPDS 33-0306), and thenardite (sodium sulphate with JCPDS 37-1465). It is difficult to distinguish clearly the calcium silicate hydrate (CSH) peak at 3.04Å from the bassanite peak at 3.01Å (∼ 29.4 - 29.7° 2-theta) using XRD, with calcite also having a strong peak at 3.03Å. However, the disappearance of
the intense peak of bassanite at 6.01Å (~ 14.72° 2-theta) is an indication that a significant amount of bassanite has been dissolved and reacted (Figures 7.1 and 7.3).

The calcium silicate hydrate and thenardite can also be detected in the resultant product along with quartz and calcite at 240 days (Figure 7.3). Although significant amounts of quartz and calcite phases are present at 240 days, it can be seen by comparing with the 2 day diffractogram, that the peaks associated with these two phases are not found to be as well-defined and sharp; thereby indicating that these phases continue to react in the system over time.

The calcium silicate hydrate formed by the alkaline activation of HEM does not appear to have a highly crystalline structure, as the XRD diffractogram associated with this phase contains only 3 characteristics peaks at 1.82, 2.79 and 3.04Å. At 240 days, this CSH phase does not transform into the more crystalline form of CSH. Further evidence obtained from the SEM analysis of this material as shown in Section 7.3.3.4 will confirm the existence of the CSH phase in the geopolymer binder. Although not undertaken in the present work, thermal analysis (TGA, DTA, DSC), could also be used to determine the formation of calcium hydroxide and CSH in this system.

Figure 7.3 also shows that traces of calcium hydroxide (portlandite with JCPDS 4-0733) can be detected in the resultant product at 2 days. The intensity of these peaks attributed to the presence of portlandite, was found to decrease with time, which indicates that calcium hydroxide is not a stable phase. It is possible that calcium hydroxide forms in the binder during curing, which will further react with carbon dioxide in air to form a calcium carbonate precipitate. A proposed overall reaction that takes place during the alkaline activation of bassanite is represented by Equation 7.2:

\[
2\text{Na}_2\text{SiO}_3 + 6\text{NaOH} + 5(\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}) \rightarrow \\
2(\text{Ca}_{1.5}\text{SiO}_3\cdot 1.75\text{H}_2\text{O}) + 5\text{Na}_2\text{SO}_4 + \text{Ca(OH)}_2
\] (7.2)

It is known that the amount of gypsum dissolved into solution increases with increasing sodium hydroxide concentration (Clark and Brown, 1999). Gypsum is
therefore not expected to be found in the resultant matrix in an alkaline activated MK-HEM system. The high concentration of hydroxide ions (>2.5M) in the alkaline activated system will ensure that the soluble calcium and sulphate ions from calcium sulphate hemihydrate remain in the solution phase, instead of undergoing rapid crystallisation to form gypsum. Moreover, it is confirmed by the results presented in Chapters 4 and 5, that gypsum present in granulated blast furnace slag will be readily dissolved into the solution phase in an identical geopolymeric system with the same amount of metakaolin and alkaline activator present. Due to the high concentration of both soluble sodium and silicate (from the soluble sodium silicate used in the alkaline activator) in the system, it is reasonable to expect that sodium sulphate and calcium silicate hydrate will precipitate, in preference to the formation of gypsum.

7.3.3 Geopolymerisation in the Presence of Calcium Sulphate Hemihydrate

7.3.3.1 Effect of Increasing HEM Addition

Various amounts of calcium sulphate hemihydrate were added to a metakaolin-based geopolymeric system in this study. Table 7.3 shows that calcium sulphate hemihydrate addition of less than 20% of the combined weight of MK and HEM, results in an improvement in the compressive strength of the geopolymeric sample, while the excessive addition of HEM (60%) results in a geopolymer having a lower compressive strength. It is important to note that for all dosages of HEM, the compressive strength increases with time (7 to 28 days) and that there appears to be a maximum strength at approximately 10% addition of HEM.

XRD analysis (Section 3.4.2) was conducted on all binders at 2, 7, 28 and 240 days. Figure 7.4 shows the x-ray diffractograms of the resultant products at 2 days. The amorphous nature of the resultant material increases with increasing amount of metakaolin used in the system (i.e. decrease % of HEM). This is confirmed by the broader amorphous hump present at 18° to 35° 2-theta. Van Jaarsveld (2000) suggested that this amorphous hump is an indication of the amorphous silica, which is commonly found in samples containing an amorphous alkali aluminosilicate network. Similar XRD patterns have also been observed by other researchers as an indication of geopolymer phase formation (Phair et al., 2001, 2000).
As expected, the XRD patterns in Figure 7.4 show that the degree of crystallinity increases with increasing amount of calcium sulphate hemihydrate added (i.e. the formation of calcium carbonate increases as HEM is increased). The crystalline phases present in the resultant matrix containing 60% of HEM include calcite, quartz, thernadite, and calcium silicate hydrate. Calcite and quartz are the crystalline phases present in the raw HEM, while it is proposed that thernadite and calcium silicate hydrate are formed by the alkaline activation of calcium sulphate hemihydrate in the absence of the metakaolin, as described previously.

Similar to the matrix containing HEM alone (Figure 7.3), undissolved bassanite is unlikely to be found in the resultant matrix, which indicates that most new phases formed in the system have originated from the alkaline activation of calcium sulphate hemihydrate with metakaolin in the system. The presence of calcite and quartz indicates that the dissolution rate of calcite and quartz is much slower than that of bassanite, which makes them relatively inert or unreactive in the system investigated.

In contrast to the alkaline activation of HEM alone, calcium hydroxide could not be detected as a significant product in the system containing MK. This is possibly attributed to: (1) calcium hydroxide was not a product formed in significant quantity, (2) only amorphous calcium hydroxide was formed, or (3) calcium hydroxide readily reacted with the metakaolin. In addition, in the presence of the metakaolin there are some weakly crystalline phases found in the product, which are not observed in matrices containing HEM alone. These new phases are associated with some crystalline peaks detected at approximately 9-10° 2-theta (with d-spacing at approximately 9.9Å and 9.3Å) as shown in Figure 7.4.

In an OPC system, the aluminium and calcium ions from tricalcium aluminate (C₃A) will react with the sulphate ions from gypsum to form ettringite (calcium aluminosulphate hydrate) (Evju and Hansen, 2001; Taylor et al., 2001; Glasser et al., 1999; Taylor, 1999; Gani, 1997; Hall et al., 1996). The formation of ettringite and gypsum in a cementitious system is commonly acknowledged as the factor behind the micro-cracking and destabilisation of the CSH gel, which leads to the rapid deterioration and poor durability in modern concrete (Rodriguez-Camacho and Uribe-
According to Gollop and Taylor (1995), a broad peak at 9-10° 2-theta is attributed to a solid solution of ettringite and calcium monosulphoaluminate hydrate (the more stable form), which have a general formula of $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Ca} \cdot (\text{SO}_4) \cdot 12\text{H}_2\text{O}$ respectively. It is therefore possible that in the current system, in which calcium and sulphate sources (HEM) and aluminium source (MK) are present, the weakly crystalline peaks detected at about 9-10° 2-theta are associated with the formation of ettringite or some other unidentified phase. However, the other peaks associated with ettringite i.e. 5.61Å (15.78° 2-theta), 3.87Å (22.94° 2-theta) and 2.56Å (35.02° 2-theta) are difficult to identify in the XRD diffractogram presented (Figure 7.4); therefore it is not conclusive at this stage to confirm whether ettringite or calcium monosulphoaluminate hydrate is a product formed. Although not undertaken in the current study, it is important to note that thermal analysis (DTA, TGA) could be used to identify the formation of such phases in this system.

7.3.3.2 Effect of Aging

Figure 7.5 shows XRD diffractograms of matrices containing 20% HEM at time periods at 2, 28 and 240 days. It can been seen that the degree of crystallinity in the samples increases with time, and the intensity of the crystalline peaks with $d_{\text{spacing}}$ at approximately 9.3Å increases with time. Likewise from Figure 7.6, the XRD diffractogram of matrices containing 60% HEM indicates that the degree of crystallinity present in the resultant product increases with time. In this case, the intensity of the crystalline phase associated with $d_{\text{spacing}}$ at ~ 9.3Å increases with time, and also that of phases associated with $d_{\text{spacing}}$ at ~ 4.6Å and 4.9Å.

According to the JCPDS data, crystalline peaks with $d_{\text{spacing}}$ at ~ 4.6Å and 4.9Å are associated with ettringite formation. However, without further analysis, it is not possible to confirm the identity of the new phase based on the XRD results alone as other peaks associated with ettringite (as described in the previous section) are still difficult to be distinguished at 240 days. However, it should be noted that the XRD results confirm that gypsum is not a product formed in such systems.
7.3.3.3 Effect of Alkalinity of Alkaline Activator

Table 7.4 shows the compressive strength of samples containing 80% of MK and 20% of HEM at 2, 7 and 28 days. It is shown that the matrices synthesised using Ms = 1.5 achieve the highest compressive strength. This optimum ratio observed is postulated to be the result of the higher extent of dissolution of silicon and aluminium from metakaolin as discussed previously in Section 7.3.1. Thus, the geopolymeric gel (the alkali aluminosilicate) is postulated to be the dominant phase that governs the binding property of the matrix in the MK-HEM system.

Figure 7.7 shows the x-ray diffractograms of the matrices containing 20% HEM synthesised using different Ms at 2 and 240 days. It is observed that for the range of Ms considered, the degree of crystallinity in the resultant matrices was found to increase with time. Moreover, despite the use of an alkaline activator with a different amount of sodium hydroxide, the mineralogy of the resultant products at 240 days is more similar to each other than they are at 2 days.

Based on the observations from Figure 7.7, it is suggested that the nature of the long-term products of an alkaline activated MK-HEM system is independent of the initial alkalinity of the alkaline activator used for the range of alkalinites studied. However, the alkalinity of the alkaline activator does affect the initial reaction rates and initial products that form in the system. Subsequently, the initial phases and early products formed in the system are highly dependent on the initial alkalinity.

Figure 7.7 shows clearly that the intensity of the crystalline peak changes substantially at d-spacing ~ 9.9Å at 2 days for matrices synthesised at different Ms. This peak reaches its highest intensity for Ms = 1.5, and this coincides with results presented earlier that showed a greater extent of dissolution of aluminium (after 1h) when 5M NaOH (equivalent to the actual system of Ms = 1.5) is used. It is therefore proposed that this peak is associated possibly with ettringite, and it results from the interaction between soluble aluminium from MK and other soluble species in the system.

7.3.3.4 Microstructure of the Alkaline Activated MK-HEM Product

The microstructure morphology of the MK-HEM system was studied by scanning electron microscopy (SEM) (refer to Section 3.4.4 for sample preparation
methodology). Figure 7.8 shows the typical features found in a matrix consisting of 20% of HEM, 80% MK, and alkaline activator with Ms = 1.2 at 28 days. Figure 7.8 shows that four distinct regions can be identified in the matrix, marked as A, B, C and D respectively. Similar microstructures containing four distinct regions could also be observed in the binders synthesised using other Ms values (1.5 and 2.0).

The point-wise elemental composition (energy dispersive spectroscopy – EDS) analysis conducted randomly on the different areas of the matrix, and the summary of average elemental composition are presented in Table 7.5. It was found that the area marked A in Figure 7.8 is calcium silicate hydrate, with traces of sodium and sulphate. The area marked B is sodium silicate, with some aluminium and a small percentage of calcium and sulphate. The area marked C is some form of sodium aluminosilicate, with less than 1 mol% of calcium. The area marked D contains a substantial amount of sodium and sulphate, which is likely to be the sodium sulphate (thenardite) as detected by XRD analysis.

Figures 7.9 to 7.11 show a magnified view of the different phases in Figure 7.8. Figure 7.9 highlights the morphology of calcium silicate hydrate (A) core with the sodium silicate shell (B) around it. Outside the sodium silicate shell, the gel (C) phase was found to be porous and the elemental composition of this phase is similar to that of the geopolymeric gel in the absence of the calcium sulphate hemihydrate, but containing traces of calcium and sulphate.

Figure 7.11 shows the magnified view of the sodium sulphate formed in the reaction. This micrograph also clearly shows that the calcium silicate hydrate core (A) with the sodium silicate shell (B) around it. Sodium sulphate (D) and geopolymeric gel (C) were formed around the calcium silicate hydrate and sodium silicate. The elemental analyses of the different phases present in the resultant product (Table 7.5) show that the elemental compositions of the resultant phases are significantly different.

The molar ratio between calcium and silicon (Ca/Si) in calcium silicate hydrate (A) formed was found to be 1.49. This ratio is almost the same as 1.5, which is the theoretical Ca/Si ratio of the calcium silicate hydrate phase (JCPDS 33-0306) detected by XRD. This confirms that semi-crystalline CSH was one of the products in the
alkaline activated MK-HEM system as discussed previously. The presence of sodium and sulphate in this phase is likely to be attributed to the presence of other precipitates (e.g. sodium silicate and sodium sulphate) on the surface of the CSH gel. Xu and Sarkar (1991) found that the addition of NaOH could cause some substitution of sodium for calcium in CSH in a gypsum activated fly ash cementitious system. It is thought that a similar substitution of sodium for calcium is possible in the alkaline activated MK-HEM system presently studied.

The results presented in this Chapter have demonstrated that the semi-crystalline calcium silicate hydrate is formed as the result of the alkaline activation of calcium sulphate hemihydrate in both the absence and presence of metakaolin. Chapters 4 to 6 have also shown that a largely amorphous calcium silicate hydrate is formed if an amorphous calcium silicate source (granulated blast furnace slag – GBFS) is used in conjunction with metakaolin in a lowly alkaline environment. The semi-crystalline CSH phase formed in the system is considered to be significantly more amorphous in nature than in comparison to the CSH phase formed in the ordinary Portland cement. However, in comparison to the CSH phase formed in the MK-GBFS system, the CSH phase formed in the current work is significantly more crystalline. It is postulated that the presence of soluble calcium and sulphate ions from the alkaline activated HEM has promoted the formation of the more crystalline form of CSH phase within a MK-based geopolymeric binder in preference to the formation of Ca-based geopolymers.

Moreover, the SEM result has confirmed that there is a clear coexistence between the CSH phase and geopolymeric gel in a single binder, regardless of the initial alkalinity used in the alkaline activation. This finding contradicts earlier work on the MK-GBFS systems presented in Chapters 4 to 6, in which the nature of the resultant product in a MK-GBFS system was found to be largely dependent on the initial alkalinity of the alkaline activator used and that a similar coexistence between the CSH phase and geopolymeric gels can only be observed in a lowly alkaline environment (Ms = 2.0). Furthermore, there is no observation of any sodium silicate shell (B) around the CSH gel core (A) in separating the geopolymeric gel and CSH phase as shown in Figure 7.11 for the MK-GBFS system. It is thought that the presence of the sulphate ions would affect how calcium participates in an alkaline activated MK-based geopolymeric system. The chemical mechanism of calcium in a
MK-HEM system would therefore be different from a MK-GBFS system. It is suggested that the presence of sulphate ions would promote and enhance the formation of semi-crystalline calcium silicate hydrate within a geopolymeric gel.

Although the XRD results presented cannot be used to confirm the presence of ettringite in the geopolymeric matrix, the SEM result suggests that a large amount of perfect ettringite crystal is not one of the products formed in the system. Despite the high level of soluble calcium and sulphate available in the solution phase, the rate of dissolution of aluminate ions from MK is comparatively slow. With the high level of sodium and silicate present in the solution phase, the consumption rate of soluble calcium and sulphate through the precipitation of other phases will be greater than the supply rate of the aluminate ion. Also, soluble silicate will also be dissociated from MK in conjunction with the soluble aluminate. Thus, the soluble silicate from the MK will always compete with the soluble aluminate in attracting the calcium and sulphate ions in the soluble phase. Moreover, the dissociated aluminate and silicate ions in the gel will readily undergo geopolymerisation in the system. Hence, there is either insufficient amount of aluminate or excessive amount of silicate present in the system, which inhibits the growth of ettringite.

It has also been observed previously that ettringite produced by the reaction of CaSO$_4$.0.5H$_2$O and C$_3$A changed into monosulphate, CSH and Ca(OH)$_2$, and that under any conditions, high pH favours the presence of monosulphate rather than ettringite, with relatively high content of sulphate in the CSH and pore solution (Taylor et al., 2001). Based on these factors discussed, it is highly unlikely for ettringite crystal to form in an alkaline activated MK-HEM system. If there is any ettringite present in the resultant matrix, it will be highly unstable and will most likely convert to the more stable form of monosulphate (Evju and Hansen, 2001).

The new XRD crystalline peaks observed in the MK-HEM binder are not believed to be associated with ettringite crystals, rather it is proposed that they are associated with another solid phase consisting of aluminium, sulphate and calcium similar to ettringite, but with a high degree of substitution with sodium within the structure. Based on various crystalline peaks as detected at 9.9, 4.9 and 4.6Å, this phase is likely to be a mineral called “U phase,” which has a similar diffraction pattern and was
identified previously in cement-based systems at high alkali (Li et al., 1996, 1997). The plausible composition of the “U phase” was proposed to be 4CaO.0.9Al₂O₃.1.1SO₃.0.5Na₂O.16H₂O, belonging to the group of hexagonal layered structures like ettringite, but differing from the latter in the fact that it contained sodium between the layers and possessed a higher interlayer distance (Li et al., 1996).

7.4 Conclusion

The results presented in this Chapter have shown that the addition of small amount of calcium sulphate hemihydrate (HEM, up to 20% by mass) increases the compressive strength of the geopolymeric binder with time. This indicates that the sulphate ion (in the presence of dissolved calcium species) could have a positive effect on the mechanical property of the resultant geopolymeric products. XRD analysis and SEM microanalysis have revealed that semi-crystalline calcium silicate hydrate (CSH) and sodium sulphate were formed in a geopolymeric gel. The presence of sulphate ions has promoted the formation of crystalline CSH gel instead of the amorphous CSH gel, which was commonly found in the MK-calcium silicate and MK-calcium hydroxide systems. This also indicates that a possible sulphate attack (in the presence of dissolved calcium species) will benefit the mechanical property of geopolymers, with an improvement in compressive strength, by initiating the formation of crystalline CSH within a geopolymeric product.

Gypsum (calcium sulphate dihydrate), which was expected to form as a result of the hydration of calcium sulphate hemihydrate, could not be detected in the alkaline activated system. Based on the XRD analysis, the new phase forming in the MK-HEM system is anticipated to be a mineral called “U phase” with a plausible composition of 4CaO.0.9Al₂O₃.1.1SO₃.0.5Na₂O.16H₂O. The “U phase” was identified previously in cement-based systems at high alkali concentration; it is similar to the ettringite but differed from the latter with the presence of sodium between the layers and possessed a higher interlayer distance.

The nature of the long-term products of an alkaline activated MK-HEM system is independent of the initial alkalinity of the alkaline activator for the range of alkalinity studied, with the geopolymer product formed becoming more crystalline with time.
This suggests that despite the use of different initial alkalinity, the reaction mechanisms taking place are essentially the same. However, the alkalinity of the alkaline activator does play an important role in affecting the reaction rate at the initial stage of the geopolymerisation.

This Chapter has investigated a calcium material containing anions (i.e. $\text{SO}_4^{2-}$) other than hydroxide and silicate, the next Chapter will examine the effect of another calcium material carrying a different anionic group, carbonate in geopolymerisation.
Table 7.1: Chemical composition of metakaolin (MK) and calcium sulphate hemihydrate (HEM) in mass %.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>0.10</td>
<td>54.78</td>
<td>40.42</td>
<td>0.76</td>
<td>0.41</td>
<td>2.72</td>
<td>0.07</td>
<td>-</td>
<td>1.10</td>
</tr>
<tr>
<td>HEM</td>
<td>37.88</td>
<td>5.18</td>
<td>1.91</td>
<td>0.32</td>
<td>0.67</td>
<td>0.47</td>
<td>0.38</td>
<td>32.04</td>
<td>15.94</td>
</tr>
</tbody>
</table>

Table 7.2: Compressive strength (MPa) of geopolymeric binder (100% MK) synthesised using different SiO₂/Na₂O molar ratios (Ms).

<table>
<thead>
<tr>
<th>Ms = SiO₂/Na₂O</th>
<th>2 Days</th>
<th>7 Days</th>
<th>28 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>&lt;5</td>
<td>7.8</td>
<td>12.8</td>
</tr>
<tr>
<td>1.5</td>
<td>34.0</td>
<td>37.8</td>
<td>39.4</td>
</tr>
<tr>
<td>1.2</td>
<td>24.1</td>
<td>24.5</td>
<td>26.8</td>
</tr>
</tbody>
</table>

Table 7.3: Compressive strength (MPa) of different MK-HEM binders synthesised at SiO₂/Na₂O molar ratio = 1.2.

<table>
<thead>
<tr>
<th>MK/(MK+HEM)</th>
<th>2 Days</th>
<th>7 Days</th>
<th>28 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.1</td>
<td>24.5</td>
<td>26.8</td>
</tr>
<tr>
<td>0.9</td>
<td>28.21</td>
<td>32.3</td>
<td>35</td>
</tr>
<tr>
<td>0.8</td>
<td>25.1</td>
<td>25.7</td>
<td>27</td>
</tr>
<tr>
<td>0.4</td>
<td>9.38</td>
<td>13.4</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 7.4: Compressive strength (MPa) of binders containing 80% MK and 20% HEM synthesised at different Ms (SiO₂/Na₂O molar ratio) of alkaline activator.

<table>
<thead>
<tr>
<th>Ms = SiO₂/Na₂O</th>
<th>2 Days</th>
<th>7 Days</th>
<th>28 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>10.3</td>
<td>11.2</td>
<td>9.5</td>
</tr>
<tr>
<td>1.5</td>
<td>35.1</td>
<td>40</td>
<td>43.6</td>
</tr>
<tr>
<td>1.2</td>
<td>25.1</td>
<td>25.7</td>
<td>27</td>
</tr>
</tbody>
</table>
Table 7.5: The average elemental composition (by mole with standard derivation) and the estimated molar ratios between the major oxide components of the different major phases present in the resultant matrix synthesised from the alkaline activation of 20% of HEM and 80% using alkaline activator with Ms = 1.2 at 28 days.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>68.0±2.4%</td>
<td>62.8±3.7%</td>
<td>63.6±4.1%</td>
<td>57.8±1.5%</td>
</tr>
<tr>
<td>Na</td>
<td>5.7±5.6%</td>
<td>14.05±11.7%</td>
<td>15.8±8.3%</td>
<td>23.5±5.0%</td>
</tr>
<tr>
<td>Al</td>
<td>0±0%</td>
<td>3.2±9.2%</td>
<td>5.4±7.7%</td>
<td>2.0±22.5%</td>
</tr>
<tr>
<td>Si</td>
<td>10.2±12.7%</td>
<td>13.2±0.9%</td>
<td>12.5±4.9%</td>
<td>4.9±24.5%</td>
</tr>
<tr>
<td>S</td>
<td>1.0±10.3%</td>
<td>1.9±7.3%</td>
<td>3.0±17.6%</td>
<td>10.2±10.6%</td>
</tr>
<tr>
<td>Ca</td>
<td>15.2±6.4%</td>
<td>3.1±27.9%</td>
<td>0.7±24.7%</td>
<td>0.5±32.2%</td>
</tr>
<tr>
<td>CaO/SiO₂</td>
<td>1.49</td>
<td>0.23</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO/SO₃</td>
<td>15.2</td>
<td>1.63</td>
<td>0.23</td>
<td>0.05</td>
</tr>
<tr>
<td>Al₂O₃/SiO₂</td>
<td>0</td>
<td>0.12</td>
<td>0.22</td>
<td>0.20</td>
</tr>
<tr>
<td>Al₂O₃/Na₂O</td>
<td>0</td>
<td>0.23</td>
<td>0.34</td>
<td>0.09</td>
</tr>
<tr>
<td>Na₂O/SO₃</td>
<td>2.85</td>
<td>3.69</td>
<td>2.63</td>
<td>1.15</td>
</tr>
<tr>
<td>Number of samples</td>
<td>50</td>
<td>48</td>
<td>60</td>
<td>45</td>
</tr>
</tbody>
</table>
Figure 7.1: XRD diffractogram of calcium sulphate hemihydrate (bassanite) (Gyprock Base Coat 100).
Figure 7.2: Dissolution of silicon (Si) and aluminium (Al) from metakaolin (MK) as a function of NaOH concentration.
Figure 7.3: XRD diffractograms of alkali activated calcium sulphate hemihydrate binder synthesised at NaO/SiO$_2$ molar ratio = 1.2. (C - calcite, CSH - calcium silicate hydrate, P - portlandite, Q - quartz and T - thenardite)
Figure 7.4: XRD diffractograms of matrices synthesised with the addition of various amounts of calcium sulphate hemihydrate (HEM) with alkaline activator (Ms = 1.2) at 2 days. (C - calcite, CSH - calcium silicate hydrate, P - portlandite, Q - quartz and T - thenardite)
Figure 7.5: XRD diffractograms of matrices synthesised with 80% MK and 20% HEM, with alkaline activator (Ms = 1.2) at 2, 28 and 240 days. (C - calcite, CSH - calcium silicate hydrate, Q - quartz and T - thenardite)
Figure 7.6: XRD diffractograms of matrices synthesised with 40% MK and 60% HEM with alkaline activator (Ms = 1.2) at 2, 28 and 240 days. (C - calcite, CSH - calcium silicate hydrate, Q - quartz and T - thenardite)
Figure 7.7: XRD diffractograms of matrices containing 80% MK and 20% HEM and synthesised at different modulus (Ms = SiO$_2$/Na$_2$O) of alkaline activator at 2 and 240 days. (C - calcite, CSH - calcium silicate hydrate and T - thenardite)
Figure 7.8: The common features found in an alkaline activated MK-HEM binder. There are several different phases present in the resultant product, marked as A, B, C and D. (A – calcium silicate hydrate with traces of sodium; B – sodium silicate with some aluminium and a low % of calcium and sulphate; C – sodium aluminosilicate which is similar to the geopolymeric gel formed in the absence of calcium sulphate hemihydrate and D – sodium sulphate)
Figure 7.9: Enlarged view of the calcium silicate hydrate (CSH) (A) region and the sodium silicate shell (B) around the CSH core.
Figure 7.10: Enlarged view of the porous area of the sodium aluminosilicate (C) region.
Figure 7.11: Enlarged view of the sodium sulphate (D), other major phases (A, B, C) can also be clearly observed.
Chapter 8

The Effect of Calcite (CaCO$_3$) on Geopolymerisation

Chapters 6 and 7 have examined the effect of various calcium silicate and calcium sulphate materials on geopolymerisation. This chapter will therefore investigate the effect of calcium carbonate (a calcium containing material with a different anionic group) on geopolymerisation. Limestone rock is the common most form of calcium carbonate, which can also occur as chalk, marble, corals, calcite, aragonite, and dolomite (calcium magnesium carbonate). Limestone and dolomite are widely used as building materials and road aggregate and both are quarried on a vast scale worldwide.

The addition of either calcite (CAL, CaCO$_3$) or dolomite (DOL, CaMg(CO$_3$)$_2$) to a metakaolin (MK) based geopolymeric binder is found to improve the compressive strength with time. However, similar to other calcium-containing materials investigated so far, the excessive addition (>40 mass%) of calcite to the geopolymeric binder is found to be detrimental. In general, calcite is found to be more effective than dolomite in improving the compressive strength of a geopolymeric binder.

Chapters 4 to 7 showed that calcium silicate hydrate (CSH) formed simultaneously with a geopolymer phase, which resulted in the improvement of the mechanical strength of the final product. However, CSH could not be detected in the MK-CAL binder for the alkalinity range studied. The failure to form both CSH and a geopolymeric gel is suggested as the reason for the observed limited compressive strength exhibited by the binder at a low alkaline condition (Ms = 2.0). However, the compressive strength of a binder synthesised at Ms = 2.0 was found to rapidly increase at approximately 90 days. Even though the chemical role of calcite in geopolymerisation is limited, whereby calcite predominantly acts as a physical
filler/micro-aggregate, the compressive strength exhibited by the alkaline activated calcite binder (100% calcite) suggests that the surface of calcite may react chemically in the system. Most importantly, the carbonate on the surface of the calcite or dolomite is likely to constitute a preferential substrate for geopolymerisation (in replacing some of the molecular and/or hydroxyl group). This will therefore improve the bonding between the geopolymer and the calcite/dolomite filler, hence, improve the resultant compressive strength.


8.1 Background

8.1.1 Introduction

The carbonates comprise some 200 minerals in which plane triangular \( \text{CO}_3^{2-} \) anionic groups are linked together by intermediate cations (Battey and Pring, 1997). Calcite (naturally occurring calcium carbonate, \( \text{CaCO}_3 \)) and dolomite (naturally occurring calcium magnesium carbonate \( \text{CaMg} (\text{CO}_3)_2 \)) are two of the most abundant carbonate minerals in the environment and are of great importance in scientific research and industrial application. Readers are advised to consult the work of Battery and Pring (1997) for further information regarding calcite and dolomite, where much of the information presented in this section is obtained, unless otherwise stated.

Calcite is not the only calcium carbonate mineral found naturally. There are no less than three minerals or phases of \( \text{CaCO}_3 \). Aragonite and vaterite are polymorphs with calcite, meaning they all have the same chemistry, but different crystal structures and symmetries. Aragonite is orthorhombic, vaterite is hexagonal, and calcite is trigonal. In calcite, the structure is composed of alternating layers of carbonate ions, \( \text{CO}_3^{2-} \), and calcium ions.

Dolomite differs from calcite \( (\text{CaCO}_3) \), with magnesium ions substituting some of the calcium to give the formula, \( \text{CaMg} (\text{CO}_3)_2 \). The structure of the dolomite group is taken from the calcite group structure, in which the magnesium cations occupy one
layer by themselves followed by a carbonate layer which is followed by an exclusively calcite layer and so forth. The layering is therefore: \[ \text{Ca} | \text{CO}_3 | \text{Mg} | \text{Ca} | \text{Mg} | \text{CO}_3 | \text{Ca} \]. The size of the magnesium ions (R_i = ionic radius in 6 coordination = 72 pm) is different from calcium ions (R_i = 100 pm), and the two ions are incompatible in the same layer, thus the alternating layers of carbonate and metal occur. Due to the significant size difference between calcium and magnesium, it is more stable to group the differing sized ions into same sized layers. This ordered layering of different or non-equivalent ions causes a loss of two fold rotational axes and mirror planes that are present in the calcite group structure. Dolomite's symmetry class is bar 3 whereas the calcite group's symmetry class is bar 3 2/m. The loss of symmetry allows only simple crystal forms to be used by the dolomite group minerals.

Limestone consists mainly of calcium carbonate and is the calcium source used in manufacturing of ordinary Portland cement (OPC). Nehdi (2000) found that fine carbonate fillers such as dolomite can enhance both the flowability and stability of fresh concrete. However, the presence of MgO was found to have a detrimental effect on the mechanical properties of the resultant mortar due to the formation of magnesium silicate hydrate (MSH) and magnesium hydroxide (Mg(OH)_2) (Frigione and Sersale, 1989), which was found to have no binding property. By adding calcite directly to a cement paste, calcium aluminate carbonate hydrate (3CaO.A1_2O_3.CaCO_3.xH_2O) was found to precipitate from the CSH phase (Taylor, 1964).

An investigation into the effect of calcite and dolomite addition on a geopolymer system will demonstrate the influences of carbonate species on the role of calcium in enhancing the durability of metakaolin-based geopolymeric binders. The study of dolomite will also reveal how the presence of magnesium may affect the geopolymer system.

### 8.1.2 Dissolution of Calcite

The investigation into the effect of calcite on geopolymerisation is not possible without an understanding of calcite dissolution chemistry. The dissolution of
carbonates can only occur if the solution is thermodynamically undersaturated; pH is thus an important variable in affecting the saturation ratio (Stumm, 1992). At high pH, the dissolution of calcite is dependent on both the mass transfer properties of the medium and the kinetics of the heterogeneous reactions at the carbonate surface (Fredd and Fogler, 1998; Sjoberg and Rickard, 1984; Plummer et al., 1978). The reactants become attached at or interact with surface sites; the critical crystal bonds at the surface of the mineral have to be weakened, so that a detachment of Ca$^{2+}$ and CO$_3^{2-}$ ions on the activated surface complex into the solution can occur (Stumm, 1992). Since these rates are dependent on pH and on surface charge, it is essential to understand that the CaCO$_3$ in equilibrium with the solution at a given pH, has different concentrations of Ca$^{2+}$, HCO$_3^-$, CO$_3^{2-}$, H$^+$, OH$^-$, H$_2$O and CO$_2$(aq) and different surface charge characteristics depending on how this pH has been adjusted (Stumm, 1992). The current geopolymer system is even more complex due to the presence of Na$^+$ and different silicate and aluminate species along the interfacial region between metakaolin and calcite in an alkaline activated environment.

Based on the modelling of the surface kinetics in a calcite/water system (Stumm, 1992), it is assumed that dissociated H$^+$, OH$^-$, HCO$_3^-$ and CO$_2$(aq) are able to interact as “potential determining” species (adsorption or desorption) with CaCO$_3$(s) and affect its surface charge. In a CaCO$_3$(s), CO$_2$, H$_2$O system, where CaCO$_3$(s) (calcite) is equilibrated with P$_{CO_2}$ = constant (partial pressure of CO$_2$), the equilibrium can be described by Equation 8.1:

\[
\text{CaCO}_3(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{aq}) \quad (K = 10^{0.7}) \quad (8.1)
\]

The equilibrium constant for Equation 8.1 is obtained from Equations 8.2a to 8.2d:

\[
\text{CaCO}_3(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \quad (K_1 = 10^{-8.3}) \quad (8.2a)
\]
\[
\text{CO}_3^{2-}(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{aq}) \quad (K_2^{-1} = 10^{10.2}) \quad (8.2b)
\]
\[
\text{HCO}_3^-(\text{aq}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \quad (K_3^{-1} = 10^{6.3}) \quad (8.2c)
\]
\[
\text{CO}_2(\text{aq}) \rightleftharpoons \text{CO}_2(\text{g}) \quad (K_4^{-1} = 10^{1.5}) \quad (8.2d)
\]

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where $K = K_1(K_2K_3K_4)^{-1} = 10^{9.7}$

The equilibrium concentrations in solution of each species $H^+$, $OH^-$, $Ca^{2+}$, $HCO_3^-$, $CO_3^{2-}$ and $CO_2(aq)$ are known for a given $P_{CO_2}$. The charge balance condition (electroneutrality) of the system can be represented by Equation 8.3:

$$[Ca^{2+}] + 2[H^+] = [HCO_3^-] + [CO_3^{2-}] + [OH^-]$$  (8.3)

Upon the addition of sodium hydroxide to create an alkaline environment similar to that required in a geopolymeric system, Equation 8.3 becomes:

$$[Ca^{2+}] + 2[H^+] < [HCO_3^-] + [CO_3^{2-}] + [OH^-]$$  (8.4)

Equation 8.4 is important because it indicates that at the calcite interface (at high pH), $HCO_3^-$, $CO_3^{2-}$ and $OH^-$ will be the predominant species.

When excess amount of sodium hydroxide is added to a calcite/water system, the surface charge of the $CaCO_3$ becomes negative. Calcite surfaces can then adsorb metal cations as a function of pH. Ishikawa and Ichikuni (1984) suggested that coprecipitation of sodium and potassium with calcite was possible in a mildly alkaline environment based on an exchange mechanism on the growing crystal calcite surface. The dissolution of calcite has been studied extensively due to its importance for the understanding of carbonate geochemistry. In particular the works of Sjoberg and Rickard (Sjoberg and Rickard, 1985, 1984, 1983; Sjoberg, 1976) and Plummer et al. (1978) are of great importance to aid the current understanding of how calcite participates in geopolymerisation.

### 8.2 Experimental Procedure

Readers are advised to refer to Section 3.2 for a detailed description of the geopolymer sample synthesis. A description of all analytical techniques used in this chapter can be found in Section 3.4.
8.2.1 Materials

Metakaolin (MK) used in the study was obtained from ECC International under the brand name of MetaStar 402 with a particle size 99% <10μm. Calcite (CAL) and dolomite (DOL) were purchased from Claywork, Australia. The oxide compositions of MK, CAL and DOL (Table 8.1) were obtained by X-Ray Fluorescence (XRF) analysis, using a Siemens SRS 3000 instrument as described in Section 3.4.1. The particle size analysis using a Coulter LS130 optical size analyser (Section 3.4.6) showed that the mean particle size of MK, CAL and DOL was 1.895, 17.13 and 34.99μm respectively (Table 8.2). The summary of the mineralogical information on CAL and DOL is shown in Table 8.3. The mineralogical composition of the MK, CAL and DOL was determined by x-ray diffraction (XRD) using a PHILIPS PW 1800 machine with a Cu Kα anticathode (Section 3.4.2). Identification of various crystalline phases was achieved by comparing the diffraction patterns to JCPDS (Joint Committee on Powder Diffraction Standards) data. The XRD analysis revealed that CAL and DOL are relatively pure crystalline structures as shown in Figure 8.1. However, both CAL and DOL were found to contain a small percentage of silica and alumina, as indicated by the XRF analysis (Table 8.1).

Washed sand with average size of 2mm was used as an aggregate in the samples. Sodium silicate solution was supplied by PQ Australia, Sydney under the brand name of Vitrosol N48 (with 28.7% SiO₂, 8.9% Na₂O and 62.4% H₂O; density 1,370kg/m³). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the experiment.

8.2.2 Synthesis

Controlled geopolymeric binders were prepared in the same way as those in Chapter 6, with metakaolin being mixed with alkaline activators prepared at three different alkalinities (Ms = SiO₂/Na₂O = 2.0, 1.5 and 1.2). The mass ratio between MK and the alkaline activator used was 0.69, 0.65 and 0.61 for Ms = 2.0, 1.5 and 1.2 respectively. These ratios were selected in order to maintain consistent water and soluble silicate content in all binders.

Samples were synthesised using different mass ratios between the metakaolin (MK) and the calcium carbonate (CC) source (either calcite or dolomite). The mass ratios
used were \( CC/(MK + CC) = 0.2, 0.4, 0.6, 0.8 \) and 1. The mass ratio between the dry mix (MK and CC) and the alkaline mix (sodium hydroxide and sodium silicate solution) was the same as those used to synthesise the controlled binders. Refer to Section 3.2 for a full description of the synthesis procedure.

### 8.2.3 Shrinkage Testing

Shrinkage tests were conducted on selected samples containing calcite or dolomite. The longitudinal length of the sample was measured at 90 and 560 days. The relative shrinkage was based on the ratio between the measured length of samples at 90 or 560 days and the original length of the samples (100mm). This measure will provide a relative correlation between the shrinkage and amount of calcite or dolomite added and the alkalinity used.

### 8.3 Results and Discussion

#### 8.3.1 Effect of Calcite Addition on Mechanical Properties

Table 8.4 presents the compressive strengths of calcite containing binders synthesised using an alkaline activator of \( Ms = 1.2 \). The general trends observed from Table 8.4 are: (1) the addition of moderate amount of calcite (approximately 20% of calcite by weight) was found to have a positive effect on the binding property of the matrix (Matrix L2) with an improvement in strength over time; (2) the addition of a substantial amount (>40%) of calcite to the system resulted in a significant decrease in compressive strength of the matrix (Matrices L4 to L6); and (3) the compressive strength of all matrices were generally found to increase with time.

The further increase in compressive strength after 2 days of curing was not found to be significant, with most matrices (except for those containing mostly calcite, Matrices L5 and L6) achieving approximately 90% of the compressive strength at 560 days within the first 2 days. In cases where there are substantial amounts of calcite present (Matrices L5 and L6), these matrices reached their optimum strengths at approximately 90 days. In the case where there was only moderate amount of calcite (Matrix L2) present, the binding property of the mortar improved with time and was found to have a gradual increase in compressive strength even after 560 days of
synthesis. It is important to note that even though the compressive strength of Matrix L6 (i.e. binder containing 100% calcite) is comparatively low (~10MPa), the strength is consistent even after 560 days. It appears therefore that calcite is not chemically inert in the alkaline activated system.

By visual examination and direct measurement of the longitudinal length of samples containing substantial amounts of calcite (>60%), it was found that these matrices (Matrices L5 and L6) had decreased in length by more than 10% at 560 days. These samples are also observed to have voids on the surface with an estimated diameter of up to 2mm. Moreover, it was found that the concentration of the voids increased with increasing calcite in the system. Figure 8.2 shows the change in length of selected samples containing calcite at 90 and 560 days. The longitudinal length of Matrix L5 (MK/(MK+CAL) = 0.2) was found to decrease by more than 8% of its original length (Ms = 1.2), while for Matrix L6 (MK/(MK+CAL) = 0), the change in length was found to be more than 10% at 560 days (Ms = 1.2). In general, the observed shrinkage of mortar (from Figure 8.2) has clearly been shown to increase with increasing calcite added and with increasing alkali concentration.

The relationship between calcite addition and both compressive strength and shrinkage is presented in Figure 8.3. As discussed earlier, the optimum compressive strength was achieved with a moderate addition of calcite (Matrix L2), despite a higher degree of shrinkage being observed for Matrix L2 in comparison to Matrix L1. However, in general, the compressive strength of the MK-CAL binders decreases with increasing shrinkage of the resultant binder and this result confirms that a large degree of shrinkage will lead to the poor mechanical stability. Of interest to note from Figure 8.3, is that the degree of shrinkage is approximately linear with the mass of calcite added. In contrast, the compressive strength of MK-CAL binders appears to reduce exponentially and approaches an asymptote at approximately 10MPa. This suggests that shrinkage is not the only factor that contributes to the reduction in mechanical strength as calcite addition is increased.

The mineralogical composition of all the resultant binders was determined by x-ray diffraction analysis. Figure 8.4 shows the XRD diffractograms of the resultant matrices synthesised using Ms = 1.2 at 7 days. The XRD diffractograms in Figure 8.4
show that there is still a significant amount of undissolved calcite present in each matrix (Matrices L2 to L4). Furthermore, it is apparent that the amount of unreacted calcite increases with increasing amount of calcite added to the system as expected.

Chapters 4 to 7 showed that for an identical alkaline activated system containing MK only, an amorphous (either Na\(^+\) or K\(^+\)) alkaline aluminosilicate network (a geopolymer) was the dominant product formed. As discussed in Chapter 4, the presence of this geopolymer phase is often identified through the observation of a broad hump at around 27-35° 2-theta by XRD analysis. However, due to the presence of the crystalline peaks associated with calcite, it is not possible to clearly identify the changes in this hump attributed to the formation of the geopolymer phase for the binders investigated.

In order therefore to give a better representation of how the addition of different quantities (mass %) of calcite affects the characteristics of the resultant binder, x-ray diffractograms were plotted as the difference between the diffractograms of the resultant binder 7 days after the activation and the raw material (MK and CAL) mix at the synthesis ratio before the activation (Figure 8.5). It was calculated by subtracting the “diffractogram before activation” from “diffractogram after activation” and these “difference” diffractograms will highlight the phases creased and destroyed during the alkaline activation as described previously in Section 6.3.4.

Despite the high concentration of undissolved calcite remaining in the resultant product as shown in Figure 8.4, the processed XRD data in Figure 8.5 indicate that calcite is being consumed to some extent during the alkaline activation. This is indicated by the reduction of several peaks in the XRD patterns, which are associated with crystalline calcite. It is therefore expected that a small amount of calcium carbonate (calcite) has reacted in the system. As a general trend, the amount of calcite reacted in the system increased with increasing mass of calcite added initially.

It can be seen by Figure 8.5 that all processed “difference” diffractograms have similar characteristics regardless of the amount of calcite added (i.e. 20, 40 and 60 mass%). There is huge sharp reduction in all “difference” diffractograms starting at about 26.4 to 26.7° 2-theta, following by a gradual increase in the intensity until it
reaches a maximum at around 29.5° 2-theta and then another decrease until it reaches 35° 2-theta. The same characteristic change to the "difference" pattern was observed in Chapter 6, where the effect of different calcium silicate source on geopolymerisation was discussed. The current results indicate that despite the addition of calcite, the sodium based geopolymeric gel, which was produced in the absence of calcite, is still a major product formed.

The XRD results presented in Figures 8.4 and 8.5 also suggest indirectly that despite the presence of carbonate ions (CO$_3^{2-}$) associated with the dissolution of calcite, the calcium ions behave similarly as other dissolved calcium ions originating from other calcium sources, such as calcium silicate (Chapters 4 to 6) and calcium sulphate (Chapter 7). Dissolved calcium ions do not appear to take an active part in the synthesis of a calcium-based geopolymer, similar to the known role played by alkali cation such as Na$^+$ and K$^+$. However, based on the XRD result, it is not possible to suggest exactly how calcium ions originating from calcite will participate in the alkaline activated MK-CAL system. Given that there are no new crystalline phases identified in the final product similar to the mechanistic path proposed in Chapter 5, it is thought that calcium ions originating from calcite will either: (1) react and become part of the amorphous product at the end of the reaction (e.g. react with silicate in forming amorphous CSH phase) or (2) take part in the formation of a small amount of crystalline precipitates (e.g. Ca(OH)$_2$, which may further react with CO$_3^{2-}$ to form CaCO$_3$ again); however the presence of the precipitates is not sufficient enough to be identified by XRD.

As described earlier, the compressive strength of the alkaline activated MK binder with the addition of a moderate amount of CAL increases with time. Figure 8.6 shows the XRD diffractogram of Matrix L2 (containing 20% calcite; Ms = 1.2) at different time periods. The results show that no significant amount of new crystalline phase is formed with time (up to 360 days). It should also be noted that the amount of calcite in the binder at 360 days is similar to the amount at 7 days (Figure 8.6). This indicates that most of the calcite present in the system remains unreacted or inert even after a 1 year period.
The SEM micrograph of Matrix L2 (containing 20% CAL, 80% MK of Ms = 1.2) at 14 days is presented in Figure 8.7. This micrograph highlights the general microscopic features of this system, in which the geopolymeric gel is the major phase present in the matrix with calcium containing particles (bright particles) scattered throughout the binder. The calcium silicate hydrate (CSH), which was formed within a geopolymeric binder (Chapters 4 to 7) could not be detected in the alkaline activated MK-CAL system (Matrices L2 to L6).

Figures 8.8 to 8.11 show SEM micrographs of the MK-CAL binder (Matrix L2) at different magnification and position. In contrast to the ground granulated blast furnace slag (GGBFS) (Chapters 4 to 6), cement (Chapter 6), and calcium sulphate hemihydrate (Chapter 7) system studied, the current results (Figures 8.8 to 8.11) show no formation of a calcium silicate hydrate (CSH) phase. It is important to note that the absence of the CSH phase was also observed for other systems containing crystalline calcium silicate minerals (e.g. wollastonite) as discussed in Chapter 6.

Geopolymeric gel (Region “A”) was found to be the dominant component of the resultant binder, however, a substantial amount of calcium containing particles (as indicated by the bright regions on the micrograph) were found scattered throughout the geopolymeric gel. These calcium particles include a large amount of unreacted calcite (particle “B” as indicated by the cubic to rectangular shape with an approximate length of 10µm). The SEM result is in agreement with the XRD analysis whereby a substantial amount of calcite was found unreacted in the alkaline activation.

Other smaller sized calcium containing particles (as indicated by particles “C” and “D” on the micrographs) were also found scattered throughout the geopolymeric gel (“A”). These particles are suggested to be products similar to calcium hydroxide (“C” with size <10µm) and some form of sodium aluminosilicate material with a high proportion of calcium (“D” with size ~2µm). Moreover, some Si-rich phases (“E” with size ~20µm) with composition of more than 75mol% of Si (the remaining being oxygen) were also observed (Figures 8.10 and 8.11). Different types of particles found in the MK-CAL system were differentiated and identified using the SEM-EDS.
analysis. Table 8.5 provides a summary of the average elemental composition of all different phases (or regions) found in the MK-CAL system.

Despite the large variety of possible calcium-containing particles (e.g. calcium hydroxide "C", and sodium aluminosilicate material with a high proportion of calcium "D") throughout the geopolymeric gel, the calcium concentration of the geopolymeric gel was still found to be relatively low at 1.5mol% ± 28% (Table 8.5). This provides further support that the presence of carbonate from calcite will not induce the calcium to play a significant part in the geopolymerisation, such as by forming a calcium-based geopolymeric gel (i.e. where the Ca ion acts as a charge balancing cation to the Al in 4 coordination). The calcium present in the geopolymeric gel is therefore merely a reflection of the calcium particles present on the surface of the geopolymeric gel, rather than being part of the geopolymeric structure.

Despite the low solubility of calcite in an alkaline activated system, calcite does participate in the reaction to some extent as evidenced by the consistent compressive strength of the alkaline activated CAL binder (Matrix L6). However, due to the slow dissolution of calcium from calcite, calcite will play a more significant part as a physical filler in improving the compressive strength of the resultant binder. The main contribution to the strength of the mortar synthesised using Ms = 1.2 is therefore believed to be from the sodium based geopolymeric phase and its interaction with the calcite, which acts as a physical filler/micro-aggregate in the system.

8.3.2 Effect of Alkalinity on the MK-CAL System

Figures 8.12 and 8.13 show the variation of compressive strength with time for binders containing 20% and 40% of calcite (SiO₂/Na₂O = Ms = 1.2, 1.5 and 2.0). In all cases, the compressive strength of the matrices increased with time, with the majority of strength gain achieved in <100 days.

In this work the SiO₂/Na₂O molar ratio is varied by changing the amount of sodium hydroxide used in the alkaline activator. Therefore the amount of silicate in the system remains constant. In agreement with the results reported in Chapters 6 and 7, the matrices synthesised using Ms = 1.5 exhibited the highest compressive strength compared to Ms = 1.2 or Ms = 2.0.
The characteristics in strength development of matrices synthesised using Ms = 1.2 and 1.5 (high alkali concentration) are more similar, than those observed for Ms = 2.0 (low alkali concentration). For Ms = 1.2 and 1.5, a high percentage of the final compressive strength of the binder was achieved at the early stage of synthesis (<7 days). The strength development of the binder synthesised using Ms = 2.0 is a more gradual process (Figure 8.12). Although the difference between the final compressive strength achieved at 560 days between matrices synthesised using Ms = 2.0 (40.0MPa) and Ms = 1.2 (61.3MPa) is ~20MPa, the compressive strength recorded at 7 days for Ms = 2.0 (7.49MPa) is at least 7 times less than that using Ms = 1.5 (52.6MPa). By increasing the amount of calcite added to the system (40% of CAL), it is observed that the strength development of the binder remains similar to that with 20% of CAL (Figure 8.13). This therefore indicates that the strength development profile of the MK-CAL binder is highly dependent on the alkalinity used.

Referring to Figure 8.2, the shrinkage of the resultant binder was also found to be dependent on the amount of alkali used. In general, binders synthesised at Ms = 1.5 exhibited the least degree of shrinkage. The binder containing only metakaolin at Ms = 2.0 is found to exhibit more shrinkage (>2%) in comparison to those synthesised at other conditions (~1%). However, the difference between all MK-binders synthesised at different alkaline conditions is small compared to other MK-CAL binders.

A better understanding of how CAL addition, alkalinity, and degree of shrinkage affect strength of geopolymer binder can be obtained from Figure 8.14. For binders containing the same amount of calcite, but synthesised at different alkalinity, the degree of shrinkage follows the same trend as the compressive strength. For example, the degree of shrinkage of a MK-binder (without any calcite) increases in the order of Ms = 1.5<1.2<2.0. The same trend was also noted by the compressive strength, in which the compressive strength decreases 1.5>1.2>2.0. In MK-CAL binders (40% of CAL addition), the degree of shrinkage increases in the order of Ms = 1.5<2.0<1.2 with the compressive strength decreasing in the same order of 1.5>2.0>1.2. In general, in binders with equal amount of calcite being added initially, the compressive strength decreases with increasing shrinkage in the system.
However, at the same alkalinity, the degree of shrinkage is not the only factor which affects the resultant compressive strength. As discussed in the previous section, even though the degree of shrinkage increases with increasing initial addition of calcite, the compressive strength reaches a maximum upon a moderate addition of calcite (Matrix L2, ~20% calcite) before it decreases and approaches about 10MPa in an alkaline activated calcite-binder (Matrix L6, 100% calcite). These results suggest that the degree of shrinkage is not the only factor in affecting the compressive strength of MK-CAL binder at the same alkalinity.

X-ray diffraction analysis was used to examine the mineralogy of the resultant binders containing 20% calcite synthesised using Ms = 2.0 and 1.2 (Figure 8.15). It is shown that despite the significant difference in the final compressive strength achieved, the general XRD pattern of the resultant products remains similar. XRD diffractograms of the MK-CAL binders exhibit an amorphous hump at around 20° to 35° 2-theta. This indicates that a geopolymeric phase remained as the dominant product formed in the alkaline activated MK-CAL system, regardless of the alkalinity of the alkaline activator used. Moreover, a substantial amount of crystalline calcite remained in the structure. The formation of either crystalline or amorphous calcium silicate hydrate gel as shown in the granulated blast furnace slag (Chapters 4 to 6), cement (Chapter 6) or calcium sulphate hemihydrate (Chapter 7) system could not be observed using XRD and SEM in the MK-CAL system at any alkalinity studied.

The major difference between the XRD diffractograms of Ms = 1.2 and Ms = 2.0 at 360 days (Figure 8.15) is the presence of a crystalline phase(s) with characteristic peaks at 2.015, 2.379 and 2.757Å for binder synthesised at Ms = 1.2. However, due to the presence of an amorphous material of significant quantity, it is not possible to distinguish other characteristics peaks, which could be associated with this new crystalline phase formed with time at high alkalinity. Given that there are a large number of crystalline phases (e.g. calcium silicate (JSPDS 36-0642), calcium aluminium silicate hydroxide (JSPDS 45-1447)) that could possibly be associated with any of three characteristic peaks, further study is required to identify this phase(s). Moreover, in order to have a better understanding of the role of calcium carbonate material in geopolymerisation, the next section of work will discuss the
effect of dolomite (CaMg(CO$_3$)$_2$) addition to the current system as a replacement for calcite.

8.3.3 Effect of Dolomite Addition on Geopolymerisation

In order to have a better understanding on how the presence of calcium and carbonate affect geopolymerisation, dolomite was used as a replacement for calcite in the system. Moreover, the use of dolomite in geopolymerisation will enable a comparison between the effect of calcium and magnesium (another Group II element, alkaline earth metal) in geopolymerisation. As described earlier, dolomite differs from calcite, CaCO$_3$, with the presence of magnesium ions in the crystal structure, CaMg(CO$_3$)$_2$. In calcite, the structure is composed of alternating layers of carbonate ions, CO$_3^{2-}$, and calcium ions. In dolomite, the magnesium ions occupy one layer by themselves followed by a carbonate layer, which is then followed by another calcite layer and so forth as described in Section 8.2.1.

Figure 8.16 shows the compressive strength of the resultant binder containing dolomite rather than calcite in the system. It is shown that the compressive strength of the MK-DOL binder increases with time and that the highest compressive strength was achieved when Ms = 1.5 was used. These trends are the same as that observed in the MK-CAL binders (Sections 8.3.1 and 8.3.2). For example, the binders synthesised at a highly alkaline condition (e.g. Ms = 1.2) achieve a high percentage of their final compressive strength within a short period of time, while the strength development of those synthesised at a lower alkaline condition (Ms = 2.0) is a much slower process with a gradual strength development with time. By comparing Figure 8.16 to Figure 8.12, the compressive strengths of MK-DOL binders are found to be consistently lower than that of the MK-CAL binders at all alkaline conditions studied.

Moreover, similar to the MK-CAL system, the XRD analysis (Figure 8.17) of the MK-DOL binder reveals that a geopolymeric phase remained as the dominant product formed (as identified through the presence of an amorphous hump at around 20° to 35° 2-theta), regardless of the alkalinity of the alkaline activator used. There also remains a significant amount of unreacted dolomite in the structure.
It was suggested in Chapter 6 that the effectiveness of different crystalline calcium silicate sources to improve the compressive strength of the resultant binders was due to the physical property (e.g. hardness) of the unreacted calcium silicate particles, whereby they acted as micro-aggregate in the system. Therefore, the “harder” the unreacted calcium silicate particle, the greater observed compressive strength. Based on this principle, the MK-DOL binder is expected to exhibit a higher compressive strength than that of MK-CAL for the same synthesis conditions. Although the physical properties (e.g. hardness and average specific gravity) of both calcite and dolomite are found to be similar (Table 8.3), dolomite does have a slighter higher hardness. The consistently lower compressive strength achieved for MK-DOL is therefore most likely attributed to either (1) a lower calcium presence in the MK-DOL system or (2) different surface property (including chemical composition, atomic structure and surface morphology (e.g. sphericity/convexity/texture) of calcite and dolomite, which affects the packing characteristics of the resultant matrix.

The latter is important because the surface property of calcite and dolomite will play a role in the bonding at the particle-matrix interface, which is likely to affect the density and uniformity of the packing of geopolymeric phase in the neighbourhood of the calcite/dolomite surface similar to the cementitious system (Stroeven and Stroeven, 1999). The current results therefore suggest that calcite is a better physical filler in enhancing the structure of a geopolymeric binder than dolomite.

As shown by Glasser (1997), it is possible to have some of the available magnesium ions replacing calcium ions in calcium hydroxide (Ca(OH)$_2$) and calcium silicate hydrate (CSH), with a subsequent decrease in pH in the system. Magnesium silicate hydrate (MSH) is known to exhibit minimum (with virtually none) binding effect (Frigione and Sersale, 1989). It is possible therefore, that a substitution of Ca for Mg of some kind may also occur in the geopolymer system, however, the effectiveness of calcium over magnesium in geopolymerisation may also explain the consistently lower compressive strength exhibited by the MK-DOL under all alkalinitities.

Previous work conducted by Lee and van Deventer (2002a, b) demonstrated in a fly ash based geopolymeric system, that the ultimate strengths will increase without any apparently adverse effects, when carbonate salts (e.g. K$_2$CO$_3$, CaCO$_3$ and MgCO$_3$)
were added during synthesis. The current study has reinforced that the presence of a small amount of carbonate material will enhance the long-term strength (>360 days) of a geopolymeric product. Lee and van Deventer (2002a, b) suggested that the presence of carbonate salts, K₂CO₃ and CaCO₃, was beneficial by lowering the molecular water and/or hydroxyl content and preventing hydrolytic attack on the gel without inhibiting the formation of the geopolymeric gel. Even though the concentration of CO₃²⁻ ions in the current system is significantly lower due to the poor dissolution of calcite or dolomite in the alkaline activated system, the presence of small amounts of soluble carbonate ions in the system is likely to have a similar effect as the carbonate salt in enhancing the compressive strength of the resultant product. More importantly, the carbonate on the surface of the calcite or dolomite is likely to constitute a preferential substrate for geopolymerisation (in replacing some of the molecular and/or hydroxyl group). This will therefore improve the bonding between the geopolymer and the calcite/dolomite filler, hence, improve the resultant compressive strength.

8.4 Conclusion

The moderate addition (up to 40% by weight) of calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) was found to have a positive effect on mechanical property of the geopolymeric binder, especially in later strength development. The effect of calcite was found to be better than that of dolomite. Excessive addition of calcite to the geopolymeric gel was found to be destructive, which is likely to be caused by the significant degree of shrinkage experienced in the resultant product.

The result indicates that no calcium silicate hydrate (CSH) gel formed as the result of the alkaline activation of the MK-CAL system within the alkaline range of the alkaline activator studied. The failure to form both CSH and geopolymeric gels simultaneously has resulted in a binder with low mechanical property when lowly alkaline condition (Ms = 2.0) was used. However, the development of the compressive strength of the binder synthesised at Ms = 2.0 was found to increase rapidly after about 90 days. In contrast, the compressive strength of binders synthesised using Ms = 1.2 and 1.5 remains relatively constant after 2 days. The
current result indicates that the strength development of the MK-CAL binder is dependent on the alkalinity used.

The chemical role of calcite in geopolymerisation is limited with calcite acting similarly as crystalline calcium silicate source; i.e. as a physical filler/micro-aggregate in the system. The carbonate on the surface of the calcite or dolomite is likely to constitute a preferential substrate for geopolymerisation (in replacing some of the molecular and/or hydroxyl group). This will ultimately increase the compressive strength of the resultant matrix by improving the bonding between the geopolymer and the calcite/dolomite filler.

The thesis has so far demonstrated that the role of calcium in geopolymerisation is highly dependent on the alkalinity of the alkaline activator used in the system. The importance of alkalinity of the system is suggested to determine the rate of dissolution of the different species from the raw material, which will further determine the mechanistic path of these different species in the reaction. The importance of the dissolution step in determining the mechanistic path cannot be over-emphasised. Subsequently, a detailed study on the dissolution of the different raw material used in the thesis, with the addition of EDTA which will form calcium complexes, in affecting the dissolution rate of calcium in geopolymerisation will be presented in the next Chapter.
Table 8.1: Chemical composition of metakaolin (MK), calcite (CAL) and dolomite (DOL) in mass %.

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<tr>
<th></th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
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<td>0.10</td>
<td>54.78</td>
<td>40.42</td>
<td>0.76</td>
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<td>0.1</td>
<td>0.1</td>
<td>45.75</td>
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Table 8.2: Particle size distributions of metakaolin (MK), calcite (CAL) and dolomite (DOL) as determined by the Coulter LS130 particle sizer.

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<tr>
<th></th>
<th>Mean (µm)</th>
<th>Mode (µm)</th>
<th>D₁₀ (µm)</th>
<th>D₅₀ (µm)</th>
<th>D₉₀ (µm)</th>
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Table 8.3: Mineralogy and some physical properties of calcite and dolomite
(Battey and Pring, 1997).

<table>
<thead>
<tr>
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<th>Dolomite</th>
</tr>
</thead>
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<tr>
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<td>CaCO₃</td>
<td>CaMg(CO₃)₂</td>
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<td>Chemical Name</td>
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<td>Trigonal bar 3</td>
</tr>
<tr>
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</tr>
<tr>
<td>Hardness (Mohs)</td>
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<td>3.5 – 4</td>
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<tr>
<td>Average specific gravity</td>
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<td>2.86</td>
</tr>
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</table>

Table 8.4: Compressive strength of matrices synthesised using Ms = 1.2 and
(NaOH+NaSiO₃)/(MK+CAL) mass ratio = 1.63.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>MK/ (MK+CAL)</th>
<th>Compressive Strength (MPa) with Time (Day)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>L1</td>
<td>1</td>
<td>35.41</td>
</tr>
<tr>
<td>L2</td>
<td>0.8</td>
<td>42.07</td>
</tr>
<tr>
<td>L3</td>
<td>0.6</td>
<td>23.33</td>
</tr>
<tr>
<td>L4</td>
<td>0.4</td>
<td>14.11</td>
</tr>
<tr>
<td>L5</td>
<td>0.2</td>
<td>7.95</td>
</tr>
<tr>
<td>L6</td>
<td>0</td>
<td>&lt;5.0</td>
</tr>
</tbody>
</table>
Table 8.5: SEM EDS analysis (atomic ratios, $x \pm \sigma_n$) of various phases at 14 days as shown in Figures 8.9 to 8.11. ($x =$ average atomic %, $\sigma =$ standard deviation in % and $n =$ number of sample size)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>O</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Region)</td>
<td>1.5±28%</td>
<td>20.7±12%</td>
<td>8.5±7.7%</td>
<td>12.7±7.4%</td>
<td>55.9±2.4%</td>
<td>50</td>
</tr>
<tr>
<td>B</td>
<td>14.2±9.6%</td>
<td>2.2±17%</td>
<td>1.1±4.4%</td>
<td>2.6±18%</td>
<td>79.4±1.6%</td>
<td>25</td>
</tr>
<tr>
<td>C</td>
<td>41.4±15%</td>
<td>1.0±57%</td>
<td>0.5±5.2%</td>
<td>0.9±46%</td>
<td>55.0±14%</td>
<td>30</td>
</tr>
<tr>
<td>D</td>
<td>3.06±36%</td>
<td>20.9±42%</td>
<td>5.4±44%</td>
<td>11.5±37%</td>
<td>58.5±8.5%</td>
<td>28</td>
</tr>
<tr>
<td>E</td>
<td>0.31±54%</td>
<td>75.1±12%</td>
<td>0±0%</td>
<td>1.7±42%</td>
<td>25.4±32%</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 8.1: XRD diffractograms of calcite (CAL) and dolomite (DOL). C and D indicate the major XRD characteristic peaks of calcite and dolomite respectively.
Figure 8.2: The relative longitudinal length of the resultant binder at 90 and 560 days to its original length of the matrix synthesised at different Ms.
Figure 8.3: The compressive strength (bar chart) and relative longitudinal length (line chart) of Matrices L1 to L6 at 90 and 560 days respectively.
Figure 8.4: XRD diffractograms of binders (Matrices L2 to L4) synthesised with various quantities of calcite (CAL) using Ms = 1.2 at 7 days.
Figure 8.5: Difference between XRD diffractograms of reacted binders (Matrices L2 to L4) and XRD diffractograms of unreacted mixtures synthesised with various quantities (mass%) of calcite (CAL) using Ms = 1.2 at 7 days.
Figure 8.6: XRD diffractograms of matrices synthesised with 20 mass% calcite (Matrix L2) at different time (Ms = 1.2).
Figure 8.7: SEM micrograph of Matrix L2 synthesised with 20% calcite and Ms = 1.2 at 14 days.
Figure 8.8: SEM micrograph of Matrix L2 synthesised with 20% calcite and Ms = 1.2 at 14 days. A – geopolymeric gel; B – raw calcite with traces of silica and alumina; C – calcium precipitates including calcium hydroxide (<10μm); D – scattering of sodium aluminosilicate material with a high proportion of calcium (~2μm).
Figure 8.9: The scattering of calcium precipitates ("C") and sodium aluminosilicate material ("D") present in the MK-CAL binder as observed in Figure 8.8 are highlighted. A – geopolymeric gel; B – raw calcite with traces of silica and alumina.
Figure 8.10: SEM micrograph of Matrix L2 synthesised with 20% of calcite and Ms = 1.2 at 14 days. This particular micrograph shows the presence of Si-rich phase “E” in the binder with “D” being the sodium aluminosilicate material with a high proportion of calcium.
Figure 8.11: The Si-rich phase "E" present in the MK-CAL binder is further magnified with "D" being the sodium aluminosilicate material with a high proportion of calcium.
Figure 8.12: Compressive strength of matrices synthesised with 20% calcite and 80% metakaolin using alkaline activators of different Ms values.
Figure 8.13: Compressive strength of matrices synthesised with 40% calcite and 60% metakaolin using alkaline activators of different Ms values.
Figure 8.14: The compressive strength (Bar Chart) and relative longitudinal length (Θ) of matrices synthesised using 0%, 20% and 40% addition of calcite at various Ms conditions.
Figure 8.15: XRD diffractograms of matrices synthesised with 20% calcite and using different Ms at 360 days. The processed “difference” diffractogram highlights the difference between the diffractograms of binders synthesised using Ms = 2.0 and 1.2.
Figure 8.16: Compressive strength of matrices synthesised with 20% dolomite and 80% metakaolin, and alkaline activator with different Ms values.
Figure 8.17: XRD diffractogram of matrices synthesised with 20% or 40% of dolomite (DOL) at Ms = 2.0 and 1.2.
Chapter 9

Effect of EDTA on the Role of Calcium in Geopolymerisation

Chapters 4 to 8 have examined the effect of different calcium sources on the geopolymerisation process. Dissolution was suggested to be the first step to occur in geopolymerisation. This chapter will focus on the effect of EDTA (Ethylenediaminetetraacetic acid) on the role of calcium in geopolymerisation, especially its influence on the dissolution process and the subsequent reactions that involve calcium.

EDTA is a chelating agent widely used in analytical chemistry. In this chapter, EDTA is used to form metal complexes with calcium (Ca), aluminium (Al) and to a lesser extent with the non-metallic silicon (Si). It is found that the extent of dissolution of calcium from various calcium sources (including calcium silicate and calcium sulphate) is strongly dependent on the amount of EDTA present, and that the extent of dissolution of Ca, Al and Si increases with increasing concentration of EDTA. It is found that EDTA has a higher tendency to form a complex with each species in the order of Ca>Al>Si in an alkaline environment, irrespective of the type of calcium source used.

It is also found that the formation of Ca-EDTA complexes increases with increasing amount of EDTA added. The rapid increase in the concentration of soluble Ca species dissociated from various calcium sources appears to promote the formation of a precipitate, having a higher concentration of calcium and silicon in a highly alkaline environment. However, the nucleation growth of calcium silicate hydrate (CSH) gel along with a geopolymeric phase is not promoted and is not observed.

9.1 Background

9.1.1 Introduction

Chapters 4 to 8 have examined the effect of different calcium sources (calcium silicate, calcium sulphate and calcium carbonate) on geopolymerisation. It was found that calcium plays a prominent role in affecting the reactions that take place in the alkaline activation of metakaolin. Dissolved calcium species present in the system were found to initiate the nucleation growth of calcium silicate hydrate (CSH) gel in a geopolymeric binder, as described by the chemical mechanism proposed in Chapter 5. The coexistence of both CSH and geopolymeric gels was found to benefit the mechanical property of the resultant binder. It was proposed further in Chapters 6 to 8 that the role of calcium in geopolymerisation is dependent on the type of calcium source and alkalinity used in the system. The dissolution of silicate and aluminate species from various aluminosilicate sources is commonly believed to be the first step in geopolymerisation with or without the presence of calcium. In the presence of calcium source, the nucleation growth of CSH is believed to be controlled by the initial concentration of dissolved Si, Al and Ca species in the alkaline environment, which is further dependent on the initial rate of dissolution from source materials as suggested earlier.

The dissolution step in geopolymerisation is a complex process. The dissolution rate of minerals is commonly believed to be controlled by the chemical species present at the surface, and to a lesser extent, the size, shape, protonation and the characteristics of the dissolving surface (Brady and House, 1996). As discussed in Chapters 7 and 8, the presence of a foreign anionic species such as SO₄²⁻ or CO₃²⁻, could have a significant influence over the reactions that take place during geopolymerisation in the presence of a calcium source. A calcium chelating agent, ethylenediaminetetraacetic acid (EDTA), will be used in this chapter to examine its effect on the dissolution of Ca, and to a lesser extent on Al and Si from source materials, and the impact on the
subsequent reactions in a highly alkaline activated system. Previous research has shown that the presence of EDTA is expected to enhance the dissolution of a range of calcium materials (Fredd and Fogler, 1998), this therefore enables the study of the role of calcium in a system, where geopolymerisation and dissolution of calcium material are the two dominant reactions.

9.1.2 EDTA Complexation Chemistry

This section provides an overview of EDTA complexation chemistry, which will aid readers who are not familiar with this specialised subject. Readers are advised to consult the works of Welch (1961) and Pribil (1972) for a detailed discussion on EDTA chemistry.

Calcium chelating agents have been shown to increase the rate of dissolution of a wide range of calcium-containing materials (Fredd and Fogler, 1998). It was suggested that the formation of a calcium complex by the addition of a chelating agent will decrease the calcium ion activity and, thereby, lead to an increase in the rate of dissolution (Fredd and Fogler, 1998). Oxygen chelates such as EDTA are of great importance in analytical chemistry. EDTA is also often used in industry to selectively bind metal ions, so that these ions can be removed or cannot be reacted in undesirable ways (e.g. removing calcium ions from hard water).

EDTA has the ability to form complexes with virtually all metal ions found in the periodic table and it is well known that EDTA has a high tendency to form metal complexes with Ca and Al. However, it is thought that EDTA has a low tendency to complex a non-metal like Si. In the presence of divalent or trivalent metal ions, a water-soluble neutral or anionic metal chelate is often formed. The metal is largely prevented from reacting with competing anions and its solubility is greatly increased (Welcher, 1961).

The EDTA molecule (Figure 9.1a) has six potential sites for bonding metal ions: four carboxyl groups and two amino groups, each of the latter with an unshared pair of electrons (Skoog, et al., 1996). EDTA is therefore often viewed as a hexadentate ligand, and is often assigned with the formula, H$_4$Y. The dissociation constants for the acidic groups in EDTA are $K_1 = 1.02 \times 10^{-2}$, $K_2 = 2.14 \times 10^{-3}$, $K_3 = 6.92 \times 10^{-7}$ and
K₄ = 5.50 x 10⁻¹¹ (Skoog, et al., 1996). It was suggested that the first and second protons are removed from opposite ends of the molecule, which then approximates two dibasic acids (Welcher, 1961). As a consequence of their physical separation, the negative charge created by the first dissociation does not greatly affect the removal of the second proton. Subsequently, the first two dissociation constants are of a similar order of magnitude (Skoog, et al., 1996). The disodium salt of EDTA is one of the most frequently used EDTA salts in analytical chemistry. It has a molecular structure as shown by Figure 9.1b, which is often abbreviated with the formula, Na₂H₂Y.2H₂O.

The disodium EDTA salt (with a chemical formula and molecular weight of [CH₂.N(CH₂.COOH).CH₂COONa]₂.2H₂O and 372.24g/mol respectively) is moderately soluble in water, and a 0.1M solution has a pH of approximately 5. It behaves as a moderately weak acid (Welcher, 1961). The disodium EDTA salt is chosen as the EDTA source used in the thesis, because with the high concentration of sodium present in the current system (from the alkaline activator), the effect of sodium from the EDTA salt can be ignored.

EDTA has a unique property in that it reacts stoichiometrically and instantaneously with nearly every metal ion with which it chelates. That is, EDTA forms 1:1 complexes under ordinary conditions with most cations, including calcium and aluminium. In the current study, H₂Y²⁻ ion (from Na₂HY – disodium EDTA salt) is the complex forming species in aqueous solution. This ion reacts with the available cations (Mⁿ⁺) in the solution phase according to Equations 9.1 to 9.3 (Welcher, 1961):

\[ M^{2+} + H_2Y^{2-} \Leftrightarrow MY^{2-} + 2H^+ \]  
(9.1)

\[ M^{3+} + H_2Y^{2-} \Leftrightarrow MY^- + 2H^+ \]  
(9.2)

\[ M^{4+} + H_2Y^{2-} \Leftrightarrow MY + 2H^+ \]  
(9.3)

The complexation reaction can be generalised by Equation 9.4 as follows:

\[ M^{n+} + H_2Y^{2-} \Leftrightarrow MY^{(n-4)} + 2H^+ \]  
(9.4)
In all cases, one mole of the complex-forming ion \((H_2Y^{2-})\) reacts with one mole of metal ion \((M^{n+})\) regardless of its valence (Welcher, 1961). The three-dimensional structure of the metal-EDTA complex can be represented by Figure 9.1c, with \(M\) = any divalent or trivalent metal. The effectiveness (or stability) of EDTA as a chelate for a particular metal ion is given by its stability (or formation) constant with the metal ion. The stability constant, \(K\), can be expressed as:

\[
\frac{[MY^{n-4}]}{[M^{n+}] \times [Y^4^+]} = K
\]  

(9.5)

Table 9.1 presents the stability constants of EDTA-metal complexes of major interest in the thesis. The efficiency of complex formation with EDTA is affected by a variation in the pH of the solution. Welcher (1961) suggested that the two dominant factors in affecting the pH upon complex formation are (1) ionisation of the metal complex (low pH effect), and (2) metal ion hydrolysis effect (high pH effect). Welcher (1961) further suggested that the concentration of the EDTA is determined by the pH of the solution. Consequently, a decrease in pH will decrease the concentration of the complexing species. Thus, metal-EDTA complexes are most effective in basic solution, and a decrease in pH results in increasing ionisation, and ultimate loss of efficiency in strongly acidic solutions.

In the complexation of calcium and magnesium, the complexing efficiency of EDTA does not decrease appreciably until the pH of the solution is relatively low. It was found by Welcher (1961) that a slight loss of complexing efficiency is observed when the pH drops below 7.5. However, at pH below 5, most calcium complexes will precipitate as calcium oxalate (Welcher, 1961).

There is an increasing tendency for the formation of metal hydroxides with increasing pH as described in Chapter 5. The overall equation of the process and the new stability constant \((Kb)\) may be described by Equations 9.6 and 9.7 as follows:

\[
MY^{n-4} + n\text{OH}^- \Leftrightarrow M(\text{OH})_n + Y^{n-4}
\]  

(9.6)
\[
\frac{[\text{M(OH)}_n] \times [\text{Y}^{n-4}]}{[\text{MY}^{n-4}] \times [\text{OH}^-]^a} = K_b
\] (9.7)

The increase in the concentration of hydroxyl ions (OH\(^-\)) will shift the equilibrium to the right (Equation 9.6), which will increase the tendency for the precipitation of metal hydroxide species. The complexing efficiency will subsequently be reduced with increasing pH. Thus in general, \(H_2\text{Y}^{2-}\) or \(\text{Y}^{4+}\) is the major component in solution at moderately acidic media (pH 3 to 6) and alkaline environment (pH > 10) respectively (Skoog, et al., 1996).

The complexation of aluminium with EDTA is more complicated than calcium, as discussed in detail by Welcher (1961) and Pribil (1972). Soluble aluminium compounds yield precipitates of aluminium hydroxide (Al(OH)\(_3\)) as the pH of the solution is increased (from an acidic environment), and precipitation is complete in a weakly acidic solution as shown in the phase diagram in Figure 9.2. Furthermore, if an excess of sodium hydroxide is added (in an alkaline environment), the precipitate (Al(OH)\(_3\)) dissolves to form the aluminate ion (Al(OH)\(_4^-\)) (Figure 9.2).

If EDTA is added to the aluminium-containing solution in an alkaline environment, Al(OH)\(_3\) dissolves when the pH of the solution is increased, even though there is insufficient OH\(^-\) present to form Al(OH)\(_4^-\). That is upon the addition of EDTA, the stability region of Al(OH)\(_3\) will be narrowed, as represented by the modified phase diagram in Figure 9.3. When a sufficient amount of OH\(^-\) is present to promote the formation of Al(OH)\(_4^-\), all aluminium species (present in any form), including the complexed Al-EDTA species in the system, will be released and converted to Al(OH)\(_4^-\). If sufficient EDTA is present there is little, if any, Al(OH)\(_3\) formed at any stage in the change in pH of the solution.

It is anticipated in the current work that EDTA will undergo complexation reactions with calcium and aluminium, which may therefore inhibit the growth of geopolymeric and/or calcium silicate hydrate gels. Moreover, the mildly acidic nature of EDTA is likely to affect the pH of the alkaline activated system. This will ultimately affect: (1) the extent of dissolution of Si, Al and Ca species from various source materials as
demonstrated in Chapters 6 to 8, and (2) the stability of various products formed in the system, such as calcium silicate hydrate or calcium hydroxide as discussed in Chapter 5.

A study therefore of the effect of EDTA on geopolymerisation, will further demonstrate the effect of different calcium species present in the geopolymerisation. This will demonstrate: (1) the importance of calcium in controlling the reactions that take place in a geopolymeric system at the early stage; (2) its significance in determining the structure of geopolymeric products; and (3) further verify the chemical mechanism that involves calcium, as proposed in Chapter 5.

9.2 Experimental Procedure

Readers are advised to refer to Section 3.2 for a detailed description of the synthesis conditions used to form geopolymer samples. A detailed description of all analytical techniques (including compressive strength testing, XRD, SEM and ICP) used in this chapter can be found in Section 3.4.

9.2.1 Materials

The disodium salt of EDTA was manufactured by Merck. An XRD diffractogram of EDTA is presented in Figure 9.4. Analytical grade calcium oxide (AnalaR), calcium hydroxide (ICN Biomedicals Inc.), aluminium hydroxide (Merck) and aluminium oxide (AnalaR) were used as elemental standards for calcium and aluminium in the dissolution work. Silica fume (Independent Cement, Australia) was used as the elemental standard for silicon in the dissolution work. The sodium silicate solution used was supplied by PQ Australia under the brand name of Vitrosol N48 (with 28.7% SiO₂, 8.9% Na₂O and 62.4% H₂O; density 1370kg/m³). Sodium hydroxide pearl (99% purity) was purchased from Orica Australia. Distilled water was used throughout the experiment.

Metakaolin (MK) used in the synthesis was obtained from ECC International under the brand name of MetaStar 402 with a particle size <10μm. The calcium sources (CA) used have been separated into 3 different groups: (1) processed calcium silicate
sources (i.e. granulated blast furnace slag (GGBFS), cement (CEM)); (2) crystalline calcium silicate sources (i.e. wollastonite (WOL)), and (3) calcium carbonate source (i.e. calcite). These calcium sources have been described in detail in Chapter 3. The oxide compositions of commercial metakaolin and all calcium sources used are shown in Table 9.2. The particle size distribution of each material is presented in Table 9.3. The mineralogy and some physical properties of wollastonite and calcite can be found in Table 9.4.

9.2.2 Dissolution Test Work
The dissolution test work performed to determine the leachability of Si, Al and Ca from various calcium silicate sources has been discussed in Chapter 6. This chapter will revisit and further discuss some of the dissolution results, which are of relevance to this chapter. However, readers are advised to refer to Section 6.2.3.1 for the detailed description on how the standard dissolution testing (without the addition of EDTA) was conducted.

To study the effect of a complexation agent on the dissolution of MK and different calcium sources, EDTA was added to the dissolution cells at different concentrations. The following two different methods were used for the addition of EDTA:

Leaching I:
Concentrated suspensions were prepared with different concentrations (2.5, 5 and 7.5M) of sodium hydroxide. The suspension contained 50g of solid in 100mL solution of each alkali concentration. Suspensions were mixed for 1, 2, 4, 8 and 24h before centrifuging, filtrating and diluting with 10% conc. HCl prior to analysing the elemental concentrations of Ca, Si and Al by ICP-OES. The clear liquid obtained after centrifugation was filtered through a 0.2μm Minisart® membrane filter from Sartorius AG Germany to remove the suspended solid.

Similar dissolution tests were also performed, whereby after 24h, either 2g (Mass(EDTA)/Mass(solid) = 0.04) or 10g (Mass(EDTA)/Mass(solid) = 0.2) of EDTA was added to the system for 10 minutes. A sample for ICP analysis was then prepared following the same procedure as described above.
Leaching II:
Dissolution tests were conducted using suspensions containing 50g of solid in 100mL solution at various alkali concentrations and with the addition of either 1g, 2g or 10g of EDTA. Suspensions were then mixed for 1, 2, 4, 8 and 24h prior to analysing the elemental concentrations of Ca, Si and Al with ICP-OES.

9.2.3 Synthesis
Samples were synthesised using a MK/(MK+CA) mass ratio of 0.8 with MK and CA being the amount of metakaolin and other calcium materials used respectively. This particular ratio was chosen because it was found to give consistently high compressive strength results, as shown in Chapters 4 to 8. The alkaline activator solution (sodium hydroxide and sodium silicate solution) had \( M_s = \frac{SiO_2}{Na_2O} = 1.2 \) and the mass ratio between the dry mix (MK and CA) and the activator was 0.61. These specific conditions were selected in this work because it is known from previous chapters that geopolymerisation will be the dominant reaction to take place in the system. This therefore enables the study of the role of calcium in a system, where geopolymerisation and dissolution of calcium material will be the two dominant reactions.

The following five calcium sources were used in the synthesis of the geopolymer samples: granulated blast furnace slag, cement, wollastonite, calcite, and calcium hydroxide (Table 9.5). Control binders were also prepared without the addition of EDTA. It should be noted that none of the binders synthesised in the current work contained washed sand.

The synthesis of the control binder (without the addition of EDTA) and also those containing EDTA follows the standard synthesis procedure as described in Section 3.2. For the latter, a set amount of EDTA with an equivalent Mass(EDTA)/Mass(dry calcium source ratio) of either 0.04 and 0.2, which is identical to the Mass(EDTA)/Mass(dry calcium source) ratio used in the dissolution experiment is added and mixed thoroughly with the alkaline activator, prior to mixing with the dry mix.
9.3 Results and Discussion

9.3.1 Effect of EDTA on the Dissolution of Metakaolin

The addition of EDTA is expected to have a significant impact on the dissolution of aluminium and silicon from MK due to its ability to form metal complexes as discussed in Section 9.1.2. The results obtained for the dissolution of Si and Al from MK using 7.5M NaOH containing various amounts of EDTA are presented in Table 9.6. It is shown that the dissolution of Si and Al from MK reaches a maximum at approximately 4h, regardless of the amount of EDTA added. The concentration of both silicon and aluminium in solution then proceeds to decrease with time. It should be noted that the decrease in the concentration of Al was found to be more significant than that of Si when 10g of EDTA was used.

It is also shown by Table 9.6 that the concentrations of Si and Al in solution decreased with increasing EDTA added. This degree of inhibition is found to increase with increasing amount of EDTA being added. The only exception is found to be when 10g of EDTA was added initially, in which the extent of dissolution of both Si and Al after up to 2h, was more than that with the addition of either no EDTA or 2g of EDTA. In order to understand the effect of EDTA on the solubility and stability of soluble Si and Al species in alkaline solution, SiO$_2$ (silica fume) and Al(OH)$_3$ were leached in a separate experiment using the same conditions. The results of this work are shown in Tables 9.7 and 9.8.

Table 9.7 shows the effect of EDTA addition on the dissolution of Si from silica fume. In general, the addition of EDTA is found to inhibit the dissolution of Si from its silica source (silicate fume) similar to that of aluminosilicate (MK) source as discussed earlier. Whereas, an 8% reduction in dissolved Si from silica fume is observed upon the addition of EDTA (i.e. Table 9.7; [Si]$_{10g \text{ EDTA}}$/[Si]$_{30 \text{ EDTA}}$ = 0.92), this is considerably less than the 35% reduction in dissolved Si species observed in the MK system (i.e. Table 9.6; [Si]$_{10g \text{ EDTA}}$/[Si]$_{30 \text{ EDTA}}$ = 0.65) at the same conditions. Also, in contrast to reaching a maximum at about 4h in the MK-EDTA system as discussed earlier (Table 9.6), the concentration of dissolved Si from silica fume is found to increase with time (Table 9.7).
Weissbart and Rimstidt (2000) suggested that the hydrated silica in the leached layer will undergo reconstruction reactions that increase the connectivity of the network as the leached layer ages and this process further reduces the release rate of the network-formed Si species. The same phenomena could possibly be used in explaining the dissolution mechanism in MK, hence the observed concentration of dissolved Si is found to increase initially before proceeding to decrease with time. Furthermore, based on the chemical mechanism as proposed by Xu and van Deventer (2000), the presence of dissolved Al species from MK is likely to have promoted the polymerisation between various silicate and aluminate species in the alkaline medium, which is a crucial step in geopolymerisation. Subsequently, the dissolved Si will be consumed and its concentration will reduce with time. Likewise, the continuous increase in the concentration of dissolved Si from silica fume is possibly due to the absence of aluminate species in this system, where the polymerisation between dissolved silicate species alone in forming the higher ordered oligomers is slower than that of the polymerisation between both aluminate and silicate species. Therefore the dissolution of silica fume is the dominant reaction in the system, whereby the concentration dissolved Si species will increase continuously.

The dissolution of Al from Al(OH)₃ is found to increase with time in both the presence and absence of EDTA (Table 9.8). The concentration of Al species reaches a maximum when approximately 2g of EDTA is used, but the concentration of Al species with the addition of 10g of EDTA is higher than when no EDTA is added to the system. However, from the addition of EDTA to Al(OH)₃ at 24h for a further 10 minutes, the EDTA is found to be an inhibitor of the dissolution of Al species from Al(OH)₃ initially. As discussed in Section 9.1.2, if there is an excess amount of sodium hydroxide and EDTA present in the system, the Al(OH)₃ and the chelated Al-EDTA species in the system, will be released and converted to Al(OH)₄⁻. Subsequently, the addition of EDTA in the current system will promote the formation of Al(OH)₄⁻ from Al(OH)₃. This is evident from the increase in the concentration of soluble Al species as the amount of EDTA added to the system is increased. This observation is the opposite of the observed concentration of soluble Al species from MK, where the EDTA was proposed to be an inhibitor for both Si and Al species.
This reinforces the early suggestion that the presence of both Si and Al species will initiate other reactions (e.g. polymerisation) in the system.

The effect of EDTA addition on the dissolution of Si and Al from metakaolin is further examined by plotting the relative concentration of Si and Al in solution as shown in Figures 9.5 and 9.6. The relative concentration is defined as the ratio of the concentration of either Al or Si in solution in the presence of EDTA, to the Al and Si without EDTA addition. As Figure 9.5 shows, for all systems studied, the concentration of both Al and Si in the solution phase at 24h is less than that determined when no EDTA was added (i.e. relative ratio <1). Moreover, the effect of EDTA on the dissolution of Al and Si is highly dependent on the concentration of NaOH used, as shown in Figure 9.6. For system containing [NaOH] = 5M and 7.5M, it is found that the relative concentrations of both Al and Si were found to be less than 1, that is the addition of EDTA will lower the concentration of soluble Al and Si species in the system. However, the same trend was not observed for the system containing 2M NaOH. This indicates that the effect of EDTA on the dissolution of Si and Al from MK, and the solubility of different Si and Al species in solution are dependent on the concentration of hydroxide ions in solution.

In Figures 9.7 and 9.8, the average Si/Al molar ratio in different alkali solutions containing EDTA is plotted against leaching time. It is shown that the Si/Al molar ratio increases with time when the concentration of NaOH was 5 or 7.5M. However, a decrease in Si/Al ratio in solution is observed for [NaOH] = 2M (Figure 9.8). As expected, these results show that the dissolution of Al and Si in solution is dependent on the alkalinity of the NaOH used (Figure 9.8).

As discussed earlier, it was found that when 10g of EDTA was added initially, the extent of dissolution of both Si and Al at 2h was more than that with the addition of either no EDTA or 2g of EDTA. This initial enhancement (up to 4h) of the dissolution rate of MK by EDTA at high alkalinity ([NaOH] = 7.5M) as well as when low alkalinity ([NaOH] = 2M) was used could be interpreted using a surface-reaction model, where the dissolution rate is proportional to the concentration of surface species (protonated sites, de-protonated sites and mineral complexes at the mineral
From Table 9.6, it is shown that after 4h, the presence of EDTA appears to inhibit the dissolution of Si and Al from MK at high alkalinity. This is likely to be the result of the dominant polymerisation taking place between the silicate and aluminate species as discussed earlier in the section. The rapid consumption of dissolved Si and Al species in re-polymerising the aluminosilicate network (geopolymerisation) is likely to have reduced the concentration of both dissolved Si and Al species as shown in Table 9.6 with time. These results have also verified the proposed chemical mechanism as proposed in earlier chapters that the geopolymerisation is the dominant step at high alkalinity. In contrast, at low alkalinity, the dissolution of MK is much less than that at high alkalinity as shown in Chapter 6. The current results have shown that despite enhancing the dissolution of MK by adding EDTA at low alkalinity, the polymerisation between soluble Si and Al species is still slow. Subsequently, the degree of polymerisation in geopolymers formed at low alkalinity is low; thereby the compressive strength of binders containing MK alone is much weaker as demonstrated in earlier chapters. This also confirms the importance of the addition of calcium material in a geopolymeric binder in improving the resultant compressive strength at low alkalinity.

9.3.2 Effect of EDTA on the Dissolution of Granulated Blast Furnace Slag

Figure 9.9 shows the dissolution of Si, Al and Ca from ground granulated blast furnace slag (GGBFS) using 7.5M NaOH solution without the addition of EDTA. The result is also shown in Table 9.9. The concentration of dissolved Si from GGBFS in an alkaline environment was found to be higher than that of dissolved Al and Ca species at the same time period. The ratio between the concentration of dissolved Si species and the proportion of SiO₂ present in GGBFS (Table 9.9) also suggests that the relative extraction of Si from GGBFS is higher than that of Ca and Al. The concentration of Si reaches a maximum at approximately 8h of leaching before reducing gradually to a lower value. The concentration of dissolved Al in solution increases with time prior to reaching a constant value at 8h. In contrast, the concentration of calcium in solution gradually decreases as leaching progress.
Table 9.2 shows that GGBFS contains 43.0 mass% and 34.4 mass% of CaO and SiO$_2$ respectively. Despite the higher proportion of CaO present in GGBFS, the concentration of Ca in the solution phase and the relative extraction of Ca from GGBFS are much lower than that of Si (Table 9.9 and Figure 9.9). It is therefore likely that a portion of leached calcium will form Ca(OH)$_2$ and calcium silicate hydrate (CSH) precipitates in solution, as demonstrated later in the XRD analysis.

Figures 9.10 to 9.11 show the concentration profile with time of dissolved Si, Al and Ca species from GGBFS in 7.5M NaOH with various amounts of EDTA added. The most notable difference observed from the concentration profiles of the three elements of interest is calcium. The concentration of dissolved calcium in the system was found to increase substantially with increasing EDTA added to the system. This will be discussed further later in the section. In contrast, the concentration profile of Si species in alkaline solution with the addition of EDTA (up to 2g) was found to remain similar to that without any EDTA as shown in Figure 9.9. As the amount of added EDTA is increased to 10g, the concentration profile of dissolved Si tends to flatten out and remains constant with time.

Similarly, the concentration profile with time of dissolved Al species leached from GGBFS in the presence of 1g of EDTA remains similar to that obtained with no EDTA present (Figures 9.9 and 9.10). However, the concentration profile of dissolved Al leached from GGBFS was found to be increasingly different as increasing amount EDTA was used in the leaching as observed in Figures 9.10 to 9.12. This indicates that the concentration of Al in solution is dependent on the formation, stability and dissolution of other Al or non-Al compounds in the alkaline system.

In order to have a better understanding of the extent of dissolution of Si and Al from GGBFS, the relative ratio of the concentration of Al and Si species after 24h of contact between GGBFS and 7.5M NaOH with various amount of EDTA was plotted in Figure 9.13. In contrast to the results for MK as shown in Figure 9.5, the concentrations of both dissolved Al and Si species in the presence of EDTA from GGBFS are more than that obtained when no EDTA was added. The only exception
was when 1g of EDTA added initially. These results mean that the presence of EDTA in solution enhances the extent of dissolution of these compounds.

Similar to the MK system (Figure 9.8), it is also found that the effect of EDTA on the dissolution of GGBFS is highly dependent on the concentration of the NaOH used (Figure 9.14). However in this case, the relative concentrations of both Al and Si are found to be more than 1, whereas they are less than 1 in the MK system. The amount of soluble Al and Si species present in the GGBFS system at NaOH = 5M or 7.5M increases upon the addition of EDTA; but this is not observed when an alkaline activator of lower alkalinity (NaOH = 2M) was used. This confirms that the effect of EDTA on the extent of dissolution of Si and Al from GGBFS and the solubility of different Si and Al species in the alkaline activated GGBFS are highly dependent on the concentration of the hydroxide ions.

In contrast to the MK system, the presence of dissolved calcium species in the solution from GGBFS indicates that Ca\textsuperscript{2+} will play an important role in the reactions that take place in the alkaline activated system. As discussed in previous chapters, it is thought that the presence of dissolved calcium species in an alkaline activated system will lead to a range of reactions, including the precipitation of Ca(OH)\textsubscript{2} and other calcium compounds, including CSH (calcium silicate hydrate) gel. In fact, the presence of these Ca-precipitates will be shown in the XRD analysis presented later in this section. The formation of these compounds will result in the lowering of the hydroxide ion concentration (decrease the alkalinity) in the system and thereby affect the equilibrium constant, and the consumption of dissolved Si and Al species in forming other compounds, such as CSH gel or calcium aluminates.

As suggested earlier, the most notable change observed with the addition of EDTA, was the increased concentration of dissolved calcium found in the system (Figures 9.9 to 9.12). Figure 9.15 and 9.16 illustrate the substantial increase in the concentration of dissolved calcium species present upon the addition of EDTA to the system. These results are in agreement with Fredd’s (1998) finding as discussed in Section 9.1.2 that the addition of EDTA will increase the rate of dissolution of calcium-containing materials. This includes an amorphous calcium silicate, such as GGBFS, in a highly alkaline environment as demonstrated here.
To understand the effect of EDTA on the solubility and stability of dissolved calcium species in an alkaline solution with the addition of EDTA, chemical analytical grade of Ca(OH)$_2$ was leached in a separate experiment at an identical alkaline condition as GGBFS. The results presented in Table 9.10 show that EDTA increases the solubility of calcium hydroxide in a highly alkaline environment. This means that free Ca ions present in the solution phase will form a complex with EDTA in preference to the precipitation of calcium hydroxide in an alkaline activated GGBFS system.

The current results have confirmed that EDTA has the ability to increase the dissolution of Ca species from the source material and form complexes as demonstrated by the rapid increase in the concentration of dissolved Ca species when various amounts of EDTA were added to the leaching cell at the end of the 24h run for a further 10 minutes. It is suggested that the increased Ca concentration measured was mainly due to the complexes that had formed between calcium and EDTA.

Figure 9.17 shows the x-ray diffractogram of GGBFS after being leached for 24h in 7.5M NaOH containing EDTA. The XRD results show that despite EDTA addition, the leached GGBFS remains essentially amorphous, and that gypsum present in GGBFS readily dissolves upon the contact with sodium hydroxide solution. Some new crystalline phases were also formed, and these phases include portlandite (Ca(OH)$_2$) and calcium silicate hydrate (Ca$_{1.5}$SiO$_{3.5}$•xH$_2$O with JCPDS 33-0306) as suggested earlier. However, due to the highly amorphous content of the leached GGBFS, it is not possible to distinguish the presence of other crystalline phases with characteristic peaks (e.g. d-spacing at 2.017, 2.159, 2.358, 2.533 and 3.315Å). It is also clearly shown by the XRD analysis (Figure 9.17) that these new crystalline peaks were detected in the leached GGBFS in both the presence and absence of EDTA. It is concluded therefore that the alkaline activation of GGBFS alone can lead to the formation of these weakly crystalline phases (including Ca(OH)$_2$ and CSH).

By comparing the XRD analysis of the “leached” Ca(OH)$_2$ sample (Figure 9.18) to leached GGBFS (Figure 9.17), it was confirmed that despite the increase in the amount of soluble Ca being leached in the NaOH solution upon the addition of EDTA, a small amount of solid Ca(OH)$_2$ remains in the system. This is likely to be
attributed to: (1) the amount of EDTA present is insufficient to complex all Ca present, or (2) the system has reached an equilibrium that no further dissolution of Ca(OH)$_2$ could take place. Moreover, the "leached" Ca(OH)$_2$/NaOH system is unstable and is likely to react readily with the CO$_2$ in the atmosphere to form natrite (Na$_2$CO$_3$).

9.3.3 Effect of EDTA on the Dissolution of Calcium Silicate Sources with Different Crystallinity

Ordinary Portland cement (OPC) and wollastonite (WOL) are calcium silicate materials with a different crystallinity to GGBFS. In this study, they were used to understand the effect of EDTA on the dissolution of various calcium silicate sources with different crystallinity. As described in Chapter 6, OPC and WOL are semicrystalline and crystalline calcium silicate sources respectively. The concentrations of dissolved Si, Al and Ca species in alkaline solution at 24h of leaching from various calcium silicate sources are summarised in Table 9.9.

It is shown in Table 9.9, that the concentrations of both Si and Al species increase in the order of WOL<CEM<GGBFS, and that the concentration of Ca decreases in the order of WOL>CEM>GGBFS. From the XRF analysis of these three calcium silicate materials (Table 9.2), the contents of CaO, SiO$_2$ and Al$_2$O$_3$ in these materials are in the order of GGBFS<WOL<CEM, CEM<GGBFS<WOL and WOL<CEM<GGBFS respectively. In contrast to the trend observed for Al species, the extent of dissolution of Si and Ca from calcium silicate sources was not found to be dependent on the content of Si and Ca in the initial material.

Table 9.10 shows the effect EDTA addition has on the leaching of Si, Al and Ca from various calcium materials. It is shown that the EDTA addition has the most significant effect on the dissolution of Ca from each material. This is consistent with the stability constant data (Table 9.1), whereby EDTA forms more stable complexes with Ca>Al>Si in a highly alkaline environment.

Despite the observed increase in the concentration of Ca leached from wollastonite, this observed change is comparatively small in contrast to the change in the Ca concentration observed for GGBFS and CEM. The structurally ordered wollastonite
has a lower energy configuration than either cement or GGBFS, which means that wollastonite is less susceptible to hydroxide attack during the initial stage of alkaline activation. Thus, the dissolution of calcium and silicon in wollastonite is less in both the presence and absence of EDTA. This confirms that the dissolution from a crystalline calcium silicate source is less than that of amorphous or semicrystalline materials as discussed earlier in Chapter 6. From the XRD analysis of the leached wollastonite as shown in Figure 9.19, the leached wollastonite remains largely unchanged from the original raw wollastonite used (with limited change observed for the intensity of the characteristic peaks). This indicates that the dissolution of wollastonite is limited, despite the addition of EDTA. This is in agreement with the dissolution results presented earlier.

The observed increase in the concentration of leached Ca is also much greater than that observed for Si and Al species leached from GGBFS and CEM systems (with the addition of EDTA). In contrast, this difference is comparatively small in the WOL system. The XRD analysis of leached GGBFS (Figure 9.17) and CEM (Figure 9.20) shows various calcium precipitates, including different forms of calcium silicate hydrate (Ca$_{1.5}$Si$_{3.5}$·xH$_2$O, Ca$_2$SiO$_4$ and CaSiO$_3$), Ca(OH)$_2$ and other yet to be identified phases. These results confirm that the rapid dissolution of GGBFS and CEM will initiate a range of dissolution/precipitation reactions in an alkaline activated system. This is in contrast to the XRD results obtained from the wollastonite system (Figure 9.19) as discussed earlier.

The substantial increase in the concentration of leached calcium ions is an indication of the extent of dissolution that takes place in the alkaline activated GGBFS and CEM systems. The calcium dissociated from either GGBFS or CEM will be complexed readily by EDTA (provided sufficient concentration of EDTA is present). As discussed earlier, the EDTA will complex with Ca in preference to Al and Si. The presence therefore of various dissolved aluminate, silicate, sodium hydroxide and a small amount of calcium species will lead to the formation of various CSH phases and Ca(OH)$_2$ as indicated by the XRD analysis. It is expected that the rate of precipitation is dependent on the concentration of all the different species in the system. Subsequently, despite the increase in the concentration of dissolved Al and Si species
present in the system, the magnitude is small in comparison to that of dissolved Ca species.

9.3.4 Effect of EDTA on the Dissolution of Calcite

Chapter 8 suggested that the reactivity of calcite (calcium carbonate) in an alkaline environment is low, whereby limited dissolution is observed. Results from previous sections have shown that the addition of EDTA will increase the extent of dissolution of materials, so that the concentration of soluble calcium species in the solution is increased. A similar trend is also observed for the dissolution of calcite in the presence of EDTA (Table 9.10). The concentration of soluble Ca from leached calcite in an alkaline solution increases with increasing EDTA concentration. With the increasing amount of soluble Ca present in this system, it is anticipated that the concentration of free carbonate $\text{CO}_3^{2-}$ ions from leached calcite will increase simultaneously. The presence of another anionic species, carbonate $\text{CO}_3^{2-}$, in the solution did not appear to affect the complexation between Ca and EDTA as shown in the leaching results for calcite (Table 9.10). Despite the presence of carbonate ions, the concentration of dissolved calcium species increases with increasing EDTA added in the system in the same way as with other calcium silicate as discussed in previous sections.

Compared to wollastonite, the increase in the concentration of leached calcium from calcite is substantially higher. At standard conditions (neutral pH, 25°C), the published solubility constants for calcite and wollastonite are 8.35 and 12.99 respectively (Beiersdorfer et al., 2003). The CaO content in the calcite used is also found to be higher than that of wollastonite (Table 9.2). In the absence of EDTA however, the concentration of Ca species leached from wollastonite was found to be higher than that of calcite at the end of the 24h leaching period (Table 9.9). The crystal structure of the minerals is generally known to have a major effect on the dissolution mechanism and the dissolution behaviour. In fact, different models and mechanisms have been proposed to describe the dissolution of calcite and wollastonite in various systems (Kundu et al., 2003; Weissbart and Rimstidt, 2000; Fredd and Fogler, 1998; Sjoberg and Rickard, 1984). However, the dissolution behaviour and solubility of these minerals at highly alkaline condition are not readily available.
Fredd and Fogler (1998) proposed a surface complexation model detailing the enhancement of the dissolution of calcite with the addition of EDTA. In this model, the dissolution process is believed to involve the adsorption of the EDTA onto calcium sites on the calcite surface, the complexation of calcium on the surface resulting in weakening of the bonds between calcium and carbonates, and the desorption of the calcium complex and carbonate products following the Langmuir-Hinshelwood kinetics. The rate of dissolution varies considerably with pH and concentration, and it is believed to be dependent primarily on the changes in the ionic species involved in the surface chelation. However, no published model has been developed for the wollastonite-EDTA system.

9.3.5 Compressive Strength of Geopolymeric Product

Table 9.11 shows the compressive strength of the geopolymeric binders synthesised at Ms = 1.2, with different calcium sources and various amounts of EDTA added. In the absence of EDTA, the compressive strength of the various binders was found to be dependent on the calcium source used. Even though binders were prepared without the addition of an aggregate (washed sand) in this chapter, the compressive strength of binders containing processed calcium materials such as GGBFS (Matrix W1) and cement (Matrix X1) were found to be higher than the ones containing natural calcium minerals such as wollastonite (Matrix Y1) and calcite (Matrix Z1). These results follow the same trend as those prepared with the addition of an aggregate as shown in Chapters 6 and 8. However, in contrast to the compressive strength results of binders with the addition of washed sand, the general trend of the compressive strength of the binders containing a calcium source (Matrix W1, Y1 and Z1) was found to reduce with time. The compressive strengths of the standard MK-geopolymer (Matrix S1) and the binder with the addition of cement (Matrix X1) were the only two binders whose strengths were found to increase with time. This indicates that the presence of an aggregate in a geopolymeric product in the presence of a calcium source is usually required, in order to reinforce the resultant matrix to give good resistance to volume change during the drying (or hardening) stage of synthesis.

The compressive strength of binders (Matrices V1 to V3) containing Ca(OH)₂ was found to increase with increasing EDTA added as shown in Table 9.11. The compressive strength was also found to increase gradually and reach its maximum at
about 7 days, before decreasing with time. At 28 days, the compressive strength of these binders was found to be similar regardless of the amount of EDTA added initially. A similar trend was observed when calcite (calcium carbonate, Matrices Z1 to Z3) was used as the calcium source. The only difference between binders containing any of the two calcium sources is that the compressive strength of the binders containing calcite did not reach a maximum before decreasing with time.

In contrast, the effect of EDTA on the strength development of geopolymeric product containing different types of calcium silicate materials varies substantially. Binders containing cement (Matrices W1 to W3) were also found to (1) increase with increasing EDTA being added and (2) increase gradually with time regardless of the amount of EDTA being added. This trend was not observed for binders containing either GGBFS (Matrices W1 to W3) or wollastonite (Matrices Y1 to Y3). The compressive strength of these binders was found to reduce with increasing EDTA addition and with time.

Since each binder synthesised contains the same amount of MK, the current compressive strength results suggest that the addition of EDTA has exhibited different effects on geopolymeric binders depending on the type of calcium materials used. It was discussed in the previous section that the concentration of dissolved calcium species from each source increases with increasing EDTA present in the system. In the case of Ca(OH)$_2$ and calcite, calcium is the major constituent of these materials as shown in Table 9.2. The increase in the extent of dissolution of Ca from these Ca-sources leads to an increase in the concentration of dissolved calcium species present in those systems. This has a positive effect on the initial compressive strength of the resultant matrices. It is believed that the enhanced dissolution of calcium from each source results from the complexation between calcium and EDTA, will assist in the initial development of the compressive strength of a geopolymeric binder. The reduction in compressive strength of binders containing Ca(OH)$_2$ and calcite with time is likely to be due to volume changes experienced during the drying process. This is likely to induce micro-cracking throughout the binder. Further analysis in identifying the nature of various binders upon the addition of EDTA is needed in understanding the difference in compressive strength exhibited.
9.3.6 Characterisation of Geopolymeric Product with the Addition of EDTA

XRD and SEM analyses were conducted on all geopolymeric binders synthesised. The XRD and SEM results are shown in Figures 9.22 to 9.26 and Figures 9.27 to 9.29 respectively. It was found from the XRD results that the mineralogical composition of the resultant binder remains relatively unchanged despite the addition of various amounts of EDTA. A large part of the resultant geopolymer product is amorphous, similar to that synthesised without the addition of EDTA. This indicates that the addition of EDTA does not promote the significant formation of any crystalline phases (identifiable by XRD) in a MK-based geopolymeric system.

Despite the extent of dissolution of various natural calcium minerals (i.e. wollastonite and calcite) being increased upon the addition of EDTA (Sections 9.3.2 to 9.3.4), a large amount of unreacted calcite and wollastonite remained in the leached solid. The XRD analysis of the geopolymeric products containing either calcite or wollastonite (Figures 9.24 and 9.25) has confirmed that a large amount of unreacted wollastonite and calcite remained in the structure.

Figures 9.27 to 9.29 show the representative SEM micrographs of various geopolymeric products containing different calcium sources and EDTA. Figure 9.27 shows the microstructure of the MK-GGBFS binder with the addition of EDTA (Matrix W3). The geopolymeric phase was found to be the dominant phase formed in Matrix W3 despite the addition of EDTA. Based on the resultant Al₂O₃/SiO₂ and CaO/SiO₂ ratios, the geopolymeric phase synthesised resembles that formed in the absence of any calcium source or EDTA as discussed in Chapters 4 and 5. Similar to the microstructure of the MK-GGBFS binder (Matrix W1) synthesised at the same condition (Ms = 1.2), calcium precipitates ("B" with ~1µm in size) were found to be scattered in the geopolymeric product. However, particles of calcium silicate rich "C" material with a much larger size (~20µm) than what were observed previously in Chapters 4 and 5 were also found in the geopolymeric gel.

A clear phase coexistence of both geopolymeric and CSH phases similar to that observed in the MK-GGBFS at low alkalinity (Figure 5.1) is not found in Matrix W3. The rapid nucleation of CSH phase along with geopolymerisation does not take place simultaneously in this system, despite the higher concentration of soluble calcium
species present (Section 9.3.2). However, the increase in the concentration of soluble calcium from leached GGBFS may have promoted the precipitation of various calcium silicate phases in a predominant geopolymeric system to some extent. For example, precipitates containing a higher percentage of calcium and silicon based on the EDS analysis, were found scattered in the geopolymeric phase (particle "C"), as shown in Figure 9.27. Moreover, based on the elemental composition of these particles as determined by the EDS analysis, it is possible that these calcium precipitates are similar (with similar CaO/SiO₂ ratio) and are related to the CSH phase detected in the leached GGBFS by the XRD analysis (Figure 9.17). Furthermore, the geopolymeric gel formed in Matrix W3 has an average CaO/SiO₂ and Al₂O₃/SiO₂ molar ratio of 0.06 and 0.22 respectively. The value of these ratios is the same as those determined for the MK-GGBFS binder (Matrix W1) synthesised in the absence of EDTA (Chapter 5).

Figure 9.28 shows the SEM image of a geopolymeric product containing cement in the presence of EDTA (Matrix X3). A geopolymeric gel and a rich calcium silicate phase were found in the product (Figure 9.28). However, in comparison to the clear phase coexistence of geopolymer and CSH observed in the MK-CEM binder in the absence of EDTA (Matrix X1) as shown in Figure 6.7, the phase coexistence in Matrix X3 (in the presence of EDTA) is less well defined.

The geopolymeric product (Matrix Y3) containing wollastonite as the calcium source in the presence of EDTA as shown in Figure 9.29 is similar to that formed in the absence of EDTA (Matrix Y1). A significant amount of unreacted wollastonite was found remaining in the geopolymeric product with the geopolymeric gel being the dominant binding phase in the structure (Figure 9.29). Scattering of calcium precipitates with an average size of \(<5\mu m\) was formed around the geopolymeric gel. This finding is in agreement with the XRD results that a substantial amount of unreacted wollastonite remained in the structure.

9.3.7 Role of Calcium in Geopolymerisation in the Presence of EDTA

Based on the chemical mechanism as proposed in Chapter 5 for the MK-GGBFS system at high alkalinity (Ms = 1.2), the precipitation of calcium hydroxide increases with increasing hydroxide concentration in preference to the formation of CSH gel.
Subsequently, a clear coexistence between geopolymeric and CSH gels as shown in Figure 5.1 could not be observed in such conditions. This finding is in agreement with the previous findings conducted by Alonso and Palomo (2001a, b) and Puertas and Fernandez-Jimenez (2003).

A clear coexistence of both CSH and geopolymeric phases in a highly alkaline environment can only be observed when ordinary Portland cement (CEM) or calcium sulphate hemihydrate (HEM) was used in the system as demonstrated in Chapters 6 and 7 respectively. Despite the increase in the extent of dissolution of calcium sources upon the addition of EDTA as demonstrated in the present Chapter, there is no indication that the increase in the concentration of dissolved calcium species in the alkaline activated system will promote the formation of CSH gel to a greater extent. Moreover, no evidence has been found to suggest that a Ca-based geopolymer will form as the result of the increased dissolved Ca concentration in the alkaline solution. The alkaline activated MK-CEM system remains as the only system where these two phases form at a highly alkaline condition (Ms = 1.2).

The failure to form both CSH and geopolymer phases simultaneously despite the increase in the soluble Ca species in the system is likely to be due to the fact that the dissolved Ca is not in a “free” form when EDTA is present. Soluble calcium species are present as Ca-EDTA complexes (Equation 9.7) in the current system. The chemical mechanism as proposed in Chapter 5 therefore is not adequate to describe the chemical reactions that take place in the current system.

To form the CSH and geopolymer gels simultaneously, it is not only essential to have enough soluble calcium species present in the solution phase; these soluble calcium species also need to be in their “free” form, so that they can readily react and polymerise with different silicate and aluminate species in the solution phase. The failure to form CSH and geopolymeric gels simultaneously in a highly alkaline environment in the absence of EDTA is suggested to result in the rapid precipitation of calcium hydroxide in the system as described in detail in Chapter 5. In the presence of EDTA, although the extent of dissolution of the calcium source is increased, a significant proportion of the soluble Ca species present are “locked” as Ca-EDTA complexes, which are stable in an alkaline environment. The high stability
of these Ca-EDTA complexes (Table 9.1) inhibits soluble Ca to take part in any other reaction, including geopolymerisation or in the formation of CSH.

However, the current study has also indicated that the increase in the dissolution of calcium materials (by increasing the amount of dissolved calcium species present) does promote the precipitation of various calcium silicate phases in a predominant geopolymeric system to some extent. This result further supports the chemical mechanism as proposed in Chapter 5, whereby the presence of soluble Ca species in the alkaline activated system will play a significant role in determining the nature of the geopolymeric product formed.

The nature and stability of these Ca-EDTA complexes situated within a geopolymeric phase, i.e. their subsequent effect on the geopolymeric structure after an extended period, remain unclear at this stage. It is possible however to have Ca-EDTA crystals forming within the geopolymeric structure with time. Owing to the high solubility of Ca-EDTA in water, as the water molecules are released from the geopolymeric structure during the drying process, the crystallisation of Ca-EDTA is likely to take place once the saturation point is reached and this may affect the stability of binder over time.

9.4 Conclusions

It was found in the present Chapter that the extent of dissolution of Ca from various calcium sources increases with increasing concentration of EDTA. The formation of Ca-EDTA complexes increases with increasing amount of EDTA added. EDTA has a higher tendency to form a complex with Ca>Al>Si in an alkaline environment irrespective of the type of calcium source used.

Al and Si species were also found to have synchronised dissolution with Al forming metal complexes with EDTA, while the change experienced by Si upon the addition of EDTA is likely to result from the complexation between Al and EDTA in the system. Despite the apparent increase on the concentration of soluble Ca in the alkaline environment, there is no evidence that Ca will participate in
geopolymerisation as a result. Likewise, the nucleation growth of calcium silicate hydrate (CSH) gel in a highly alkaline activated geopolymeric binder was not observed. This is likely to be due to the predominant complexation reaction between Ca and EDTA. A significant proportion of the soluble Ca species present are "locked" as Ca-EDTA complexes, which are stable in an alkaline environment. The complexation between Ca and EDTA has inhibited soluble Ca to take part in any other reaction, including geopolymerisation or in the formation of CSH. Therefore a clear coexistence of geopolymeric and CSH phases has not been observed in a geopolymer binder in the presence of EDTA.
Table 9.1: Stability constants of EDTA-Metal complexes measured at 20°C and an ionic strength of 0.1.

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<td>0.6</td>
<td>-</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>WOL C</td>
<td>47.5</td>
<td>50.5</td>
<td>0.25</td>
<td>0.2</td>
<td>0.25</td>
<td>0.33</td>
<td>0.3</td>
<td>0.01</td>
<td>0.54</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcite</td>
<td>CAL D</td>
<td>53.54</td>
<td>1.48</td>
<td>0.34</td>
<td>0.21</td>
<td>1.65</td>
<td>0.33</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>42.75</td>
</tr>
</tbody>
</table>

1. A = aluminosilicate, B = Processed calcium silicate, C = Crystalline calcium silicate and D = calcium carbonate
2. LOI = Loss on ignition
Table 9.3: Particle size distribution of metakaolin (MK), ground granulated blast furnace slag (GGBFS), cement (CEM), wollastonite (WOL) and calcite (CAL) as determined by Coulter LS130 particle sizer.

<table>
<thead>
<tr>
<th></th>
<th>Mean (µm)</th>
<th>Mode (µm)</th>
<th>D_{10} (µm)</th>
<th>D_{50} (µm)</th>
<th>D_{90} (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MK</td>
<td>1.895</td>
<td>1.34</td>
<td>1.045</td>
<td>1.579</td>
<td>3.006</td>
</tr>
<tr>
<td>GGBFS</td>
<td>21.54</td>
<td>15.14</td>
<td>2.547</td>
<td>15.14</td>
<td>47.02</td>
</tr>
<tr>
<td>CEM</td>
<td>35.41</td>
<td>30.23</td>
<td>8.225</td>
<td>28.13</td>
<td>67.98</td>
</tr>
<tr>
<td>WOL</td>
<td>27.23</td>
<td>24.68</td>
<td>4.115</td>
<td>20.12</td>
<td>59.87</td>
</tr>
<tr>
<td>CAL</td>
<td>17.13</td>
<td>22.53</td>
<td>1.743</td>
<td>10.93</td>
<td>34.97</td>
</tr>
</tbody>
</table>

Table 9.4: Mineralogy and some physical properties of wollastonite and calcite

(Battey and Pring, 1997)

<table>
<thead>
<tr>
<th></th>
<th>Wollastonite</th>
<th>Calcite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>CaSiO₃</td>
<td>CaCO₃</td>
</tr>
<tr>
<td>Chemical Name</td>
<td>Calcium silicate</td>
<td>Calcium carbonate</td>
</tr>
<tr>
<td>Class</td>
<td>Silicates</td>
<td>Carbonates</td>
</tr>
<tr>
<td>Group</td>
<td>Inosilicate</td>
<td>Calcite</td>
</tr>
<tr>
<td>Crystal system (Symmetry)</td>
<td>Triclinic</td>
<td>Trigonal bar 3 2/m</td>
</tr>
<tr>
<td>Hardness (Mohs)</td>
<td>4.8</td>
<td>3</td>
</tr>
<tr>
<td>Average specific gravity</td>
<td>2.92</td>
<td>2.7</td>
</tr>
<tr>
<td>Matrix</td>
<td>Calcium Source</td>
<td>Mass (EDTA) / Mass (Calcium Sources)</td>
</tr>
<tr>
<td>--------</td>
<td>----------------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>S1(^1)</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>V1</td>
<td>Ca(OH)(_2)</td>
<td>0</td>
</tr>
<tr>
<td>V2</td>
<td>Ca(OH)(_2)</td>
<td>0.04</td>
</tr>
<tr>
<td>V3</td>
<td>Ca(OH)(_2)</td>
<td>0.2</td>
</tr>
<tr>
<td>W1</td>
<td>GGBFS</td>
<td>0</td>
</tr>
<tr>
<td>W2</td>
<td>GGBFS</td>
<td>0.04</td>
</tr>
<tr>
<td>W3</td>
<td>GGBFS</td>
<td>0.2</td>
</tr>
<tr>
<td>X1</td>
<td>Cement</td>
<td>0</td>
</tr>
<tr>
<td>X2</td>
<td>Cement</td>
<td>0.04</td>
</tr>
<tr>
<td>X3</td>
<td>Cement</td>
<td>0.2</td>
</tr>
<tr>
<td>Y1</td>
<td>Wollastonite</td>
<td>0</td>
</tr>
<tr>
<td>Y2</td>
<td>Wollastonite</td>
<td>0.04</td>
</tr>
<tr>
<td>Y3</td>
<td>Wollastonite</td>
<td>0.2</td>
</tr>
<tr>
<td>Z1</td>
<td>Calcite</td>
<td>0</td>
</tr>
<tr>
<td>Z2</td>
<td>Calcite</td>
<td>0.04</td>
</tr>
<tr>
<td>Z3</td>
<td>Calcite</td>
<td>0.2</td>
</tr>
</tbody>
</table>

\(^1\) S1 was synthesised with 100% of MK without any addition of calcium source and EDTA.
Table 9.6: Dissolution of Si and Al from MK using 7.5M NaOH solution containing different amounts of EDTA.

<table>
<thead>
<tr>
<th>Elapsed time (h)</th>
<th>NaOH only</th>
<th>NaOH + 2g EDTA</th>
<th>NaOH + 10g EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si (ppm)</td>
<td>Al (ppm)</td>
<td>Si (ppm)</td>
</tr>
<tr>
<td>1</td>
<td>2190</td>
<td>2650</td>
<td>2175</td>
</tr>
<tr>
<td>2</td>
<td>3490</td>
<td>4005</td>
<td>3460</td>
</tr>
<tr>
<td>4</td>
<td>5855</td>
<td>6620</td>
<td>5795</td>
</tr>
<tr>
<td>8</td>
<td>5330</td>
<td>5650</td>
<td>5080</td>
</tr>
<tr>
<td>24</td>
<td>5530 (1)^3</td>
<td>5075 (1)^3</td>
<td>4885 (0.88)^3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 (2g EDTA)</td>
<td>-</td>
<td>-</td>
<td>5325 (0.96)^3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>24 (10g EDTA)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1  EDTA added to the alkaline activator before being mixed with MK.

2  EDTA added to the leaching cell at 24h for 10 minutes.

3  ratio calculated based on [Si]/[Si]_{no EDTA at 24h}

4  ratio calculated based on [Al]/[Al]_{no EDTA at 24h}
Table 9.7: Dissolution of Si from silica fume (SiO₂) using 7.5M NaOH solution containing EDTA.

<table>
<thead>
<tr>
<th>Elapsed time (h)</th>
<th>Si (ppm) 0g EDTA</th>
<th>Si (ppm) 10g EDTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>388</td>
<td>a</td>
</tr>
<tr>
<td>2</td>
<td>580</td>
<td>a</td>
</tr>
<tr>
<td>4</td>
<td>829</td>
<td>a</td>
</tr>
<tr>
<td>8</td>
<td>1150</td>
<td>a</td>
</tr>
<tr>
<td>24</td>
<td>1760 (1)²</td>
<td>a</td>
</tr>
<tr>
<td>24 (10g EDTA⁻)</td>
<td>-</td>
<td>1620 (0.92)⁴</td>
</tr>
</tbody>
</table>

1  EDTA added to the leaching cell at 24h for 10 minutes.
2  ratio calculated based on [Si]/[Si]₀ EDTA at 24h
a  data are not available
Table 9.8: Dissolution of Al from Al(OH)$_3$ using 7.5M NaOH solution containing EDTA.

<table>
<thead>
<tr>
<th>Elapsed time (h)</th>
<th>Al (ppm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NaOH only</td>
<td>NaOH + 2g EDTA$^1$</td>
</tr>
<tr>
<td>1</td>
<td>3645</td>
<td>4310</td>
</tr>
<tr>
<td>2</td>
<td>5045</td>
<td>5915</td>
</tr>
<tr>
<td>4</td>
<td>7060</td>
<td>8025</td>
</tr>
<tr>
<td>8</td>
<td>9985</td>
<td>11300</td>
</tr>
<tr>
<td>24</td>
<td>13750 (1)$^3$</td>
<td>16800 (1.22)$^3$</td>
</tr>
<tr>
<td>24 (2g EDTA$^2$)</td>
<td>-</td>
<td>13550 (0.98)$^3$</td>
</tr>
<tr>
<td>24 (10g EDTA$^2$)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1 EDTA added to the alkaline activator before being mixed with dry material.
2 EDTA added to the leaching cell at 24h for 10 minutes.
3 ratio calculated based on $[\text{Al}]/[\text{Al}]_{\text{inc EDTA}}$ at 24h for Al(OH)$_3$
Table 9.9: Extent of dissolution of Si, Al and Ca after 24h of contact from various calcium sources (i.e. GGBFS, CEM, WOL and CAL) using 7.5M NaOH solution without the addition of EDTA.

<table>
<thead>
<tr>
<th></th>
<th>[Ca] (ppm)</th>
<th>[Ca]/[CaO]_source</th>
<th>[Si] (ppm)</th>
<th>[Si]/[SiO₂]_source</th>
<th>[Al] (ppm)</th>
<th>[Al]/[Al₂O₃]_source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granulated Blast Furnace Slag (GGBFS)</td>
<td>75</td>
<td>0.017</td>
<td>1990</td>
<td>0.58</td>
<td>665</td>
<td>0.47</td>
</tr>
<tr>
<td>Cement (CEM)</td>
<td>285</td>
<td>0.044</td>
<td>669</td>
<td>0.33</td>
<td>57</td>
<td>0.12</td>
</tr>
<tr>
<td>Wollastonite (WOL)</td>
<td>1090</td>
<td>0.23</td>
<td>284</td>
<td>0.056</td>
<td>16</td>
<td>0.64</td>
</tr>
<tr>
<td>Calcite (CAL)</td>
<td>301</td>
<td>0.056</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 9.10: Relative concentration of Al, Si and Ca species after 24h of contact between various types of calcium sources and 7.5M NaOH solution containing EDTA.

<table>
<thead>
<tr>
<th></th>
<th>EDTA</th>
<th>[Al]/[Al]_{No EDTA}</th>
<th>[Si]/[Si]_{No EDTA}</th>
<th>[Ca]/[Ca]_{No EDTA}</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ca(OH)₂</strong></td>
<td>0g</td>
<td></td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2g (end¹)</td>
<td>3.11</td>
<td>0.98</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>10g (end¹)</td>
<td>1.48</td>
<td>0.79</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>2g (initial²)</td>
<td>2.34</td>
<td>2.98</td>
<td>2.79</td>
</tr>
<tr>
<td><strong>Granulated Blast Furnace Slag</strong></td>
<td>0g</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2g (end¹)</td>
<td>1.36</td>
<td>0.68</td>
<td>26.20</td>
</tr>
<tr>
<td></td>
<td>10g (end¹)</td>
<td>2.77</td>
<td>1.41</td>
<td>40.93</td>
</tr>
<tr>
<td></td>
<td>1g (initial²)</td>
<td>0.92</td>
<td>1.45</td>
<td>113.07</td>
</tr>
<tr>
<td><strong>Cement</strong></td>
<td>0g</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2g (end¹)</td>
<td>3.11</td>
<td>1.40</td>
<td>18.02</td>
</tr>
<tr>
<td></td>
<td>10g (end¹)</td>
<td>10.89</td>
<td>1.58</td>
<td>49.65</td>
</tr>
<tr>
<td></td>
<td>1g (initial²)</td>
<td>1.48</td>
<td>0.91</td>
<td>6.89</td>
</tr>
<tr>
<td></td>
<td>2g (initial²)</td>
<td>2.59</td>
<td>1.73</td>
<td>12.11</td>
</tr>
<tr>
<td></td>
<td>10g (initial²)</td>
<td>8.47</td>
<td>1.81</td>
<td>41.23</td>
</tr>
<tr>
<td><strong>Wollastonite</strong></td>
<td>0g</td>
<td>1.00</td>
<td>1.00</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2g (end¹)</td>
<td>0.98</td>
<td>1.02</td>
<td>2.17</td>
</tr>
<tr>
<td></td>
<td>1g (initial²)</td>
<td>0.00</td>
<td>1.01</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td>2g (initial²)</td>
<td>0.79</td>
<td>1.13</td>
<td>1.61</td>
</tr>
<tr>
<td></td>
<td>10g (initial²)</td>
<td>2.34</td>
<td>1.64</td>
<td>2.05</td>
</tr>
<tr>
<td><strong>Calcite</strong></td>
<td>0g</td>
<td></td>
<td>2.35</td>
<td>2.79</td>
</tr>
<tr>
<td></td>
<td>2g (end¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10g (end¹)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1g (initial²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2g (initial²)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10g (initial²)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 End: EDTA was added to the leaching cell after 24h for 10 minutes.

2 Initial: EDTA was added to the alkaline activator before being poured into the dry materials initially.
Table 9.11: Compressive strength (MPa) of matrices (paste only; no sand) synthesised using 80% of MK and 20% of calcium source with various amounts of EDTA (alkaline activator of Ms = 1.2).

<table>
<thead>
<tr>
<th>Calcium Source</th>
<th>Matrix</th>
<th>Mass (EDTA) / Mass (Calcium Sources)</th>
<th>2 Days</th>
<th>7 Days</th>
<th>28 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>S1(^1)</td>
<td>0</td>
<td>24.1</td>
<td>24.5</td>
<td>26.8</td>
</tr>
<tr>
<td>Ca(OH)(_2)</td>
<td>V1</td>
<td>0</td>
<td>16.8</td>
<td>19.6</td>
<td>13.9</td>
</tr>
<tr>
<td></td>
<td>V2</td>
<td>0.04</td>
<td>18.4</td>
<td>21.0</td>
<td>12.1</td>
</tr>
<tr>
<td></td>
<td>V3</td>
<td>0.2</td>
<td>21.9</td>
<td>23.6</td>
<td>13.7</td>
</tr>
<tr>
<td>GGBFS</td>
<td>W1</td>
<td>0</td>
<td>44.0</td>
<td>41.4</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>W2</td>
<td>0.04</td>
<td>25.6</td>
<td>21.2</td>
<td>18.1</td>
</tr>
<tr>
<td></td>
<td>W3</td>
<td>0.2</td>
<td>17.8</td>
<td>19.7</td>
<td>20.4</td>
</tr>
<tr>
<td>Cement</td>
<td>X1</td>
<td>0</td>
<td>20.7</td>
<td>24.6</td>
<td>25.0</td>
</tr>
<tr>
<td></td>
<td>X2</td>
<td>0.04</td>
<td>21.9</td>
<td>21.9</td>
<td>23.0</td>
</tr>
<tr>
<td></td>
<td>X3</td>
<td>0.2</td>
<td>24.8</td>
<td>23.4</td>
<td>24.1</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>Y1</td>
<td>0</td>
<td>29.0</td>
<td>24.1</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>Y2</td>
<td>0.04</td>
<td>17.0</td>
<td>11.7</td>
<td>9.4</td>
</tr>
<tr>
<td></td>
<td>Y3</td>
<td>0.2</td>
<td>13.7</td>
<td>8.6</td>
<td>12.4</td>
</tr>
<tr>
<td>Calcite</td>
<td>Z1</td>
<td>0</td>
<td>20.8</td>
<td>18.9</td>
<td>17.6</td>
</tr>
<tr>
<td></td>
<td>Z2</td>
<td>0.04</td>
<td>21.8</td>
<td>18.1</td>
<td>18.2</td>
</tr>
<tr>
<td></td>
<td>Z3</td>
<td>0.2</td>
<td>22.5</td>
<td>22.2</td>
<td>18.8</td>
</tr>
</tbody>
</table>

\(^1\) Standard binder contains 100% MK (with no addition of any calcium source)
Figure 9.1a: EDTA molecule

Figure 9.1b: Disodium salt of EDTA molecule

Figure 9.1c: The three-dimensional structure of the metal (M = any divalent or trivalent metal) – EDTA complex.
Figure 9.2: Eh-pH diagram of the Al-Na-H₂O system at 25°C and atmospheric pressure. Al(OH)₃ is the stable phase in the range of pH ~2.5 to 12.5. (This phase diagram was calculated using a computer program HSC Chemistry for Windows Version 4.1)
Figure 9.3: Modified Eh-pH diagram of the Al-Na-H₂O system (Figure 9.2) in the presence of EDTA at 25°C and atmospheric pressure. By adding EDTA in the alkaline environment, the stability region for Al(OH)₃ will be narrowed, while the stability region Al(OH)₄⁻ will be expanded. If sufficient EDTA is present, there is little, if any, Al(OH)₃ formed at any stage in the pH change of the alkaline solution. (Solid line represents original stability boundary of different phases, while the dotted line represents the “new” stability boundary of different phase upon the addition of EDTA in the alkaline region)
Figure 9.4: XRD of EDTA
Figure 9.5: Relative concentration of Al or Si species after 24h of contact between metakaolin and 7.5M NaOH solution with the addition of various amounts of EDTA.
Figure 9.6: Relative concentration of Al or Si species after 24h of contact between metakaolin and various concentrations of NaOH solution with the addition of 10g of EDTA at the end of the 24h run for an additional 10 minutes (unless otherwise stated).
Figure 9.7: Si/Al molar ratio in solution of leached MK using 7.5M NaOH and various amounts of EDTA.
Figure 9.8: Si/Al molar ratio in solution of leached MK using different concentrations of NaOH (no EDTA added). The points highlighted represent the Si/Al ratio of species in various concentrations of NaOH with the addition of 10g EDTA for an extra 10 minutes at 24h.
Figure 9.9: Dissolution of Si, Al and Ca from ground granulated blast furnace slag (GGBS) using 7.5M NaOH solution.
Figure 9.10: Dissolution of Si, Al and Ca from granulated blast furnace slag (GGBFS) using 7.5M NaOH solution and 1g EDTA.
Figure 9.11: Dissolution of Si, Al and Ca from granulated blast furnace slag (GGBFS) using 7.5M NaOH solution and 2g EDTA.
Figure 9.12: Dissolution of Si, Al and Ca from granulated blast furnace slag (GGBFS) using 7.5M NaOH solution and 10g EDTA.
Figure 9.13: Relative concentration of Al or Si species after 24h of contact between granulated blast furnace slag and 7.5M NaOH solution containing various amounts of EDTA.
Figure 9.14: The relative ratio of the concentration of Al or Si species after 24h of contact between granulated blast furnace slag and various concentrations of NaOH solution with the addition of 10g of EDTA at the end of the 24h run for an additional 10 minutes (unless otherwise stated).
Figure 9.15: Relative concentration of Ca species after 24h of contact between granulated blast furnace slag and 7.5M NaOH solution with the addition of various amounts of EDTA.
Figure 9.16: Relative concentration of Ca species after 24h of contact between granulated blast furnace slag and various concentrations of NaOH solution with the addition of 10g of EDTA at the end of the 24h run for an additional 10 minutes (unless otherwise stated).
Figure 9.17: XRD diffractograms of leached GGBFS with various amounts of EDTA added for an extra 10 minutes after a 24-h leaching run. (Note: G - gypsum (CaSO$_4$.2H$_2$O); P - portlandite (Ca(OH)$_2$); CSH - calcium silicate hydrate (Ca$_{1.5}$SiO$_3$.5xH$_2$O, JCPDS 33-0306) and the d-spacing (Å) of the peaks associated with various unknown phase are also highlighted)
Figure 9.18: XRD diffractograms of the leached Ca(OH)$_2$ with various amounts of EDTA added for an extra 10 minutes after a 24-h leaching run.

(Note: P - Portlandite (Ca(OH)$_2$) and N - Natrite, (Na$_2$CO$_3$))
Figure 9.19: XRD diffractograms of leached wollastonite with various amounts of EDTA added for an extra 10 minutes after a 24-h leaching run. 
(Note: W - wollastonite (CaSiO₃) and the d-spacing (Å) of the peaks associated with various unknown phase are also highlighted)
Figure 9.20: XRD diffractograms of leached cement with various amounts of EDTA added for an extra 10 minutes after a 24-h leaching run. (Note: A – calcium silicate (Ca$_2$SiO$_4$, JCPDS 24-0234); B – calcium silicate (CaSiO$_3$, JCPDS 46-044); C – calcium silicate (γ-Ca$_2$SiO$_4$, JCPDS 31-0297); D – calcium silicate (α-Ca$_2$SiO$_4$, JCPDS 20-0237); F – calcium iron oxide (CaFe$_4$O$_7$, JCPDS 15-0558); G – gypsum (CaSO$_4$.2H$_2$O); P – portlandite (Ca(OH)$_2$); X – calcium silicate (Ca$_3$SiO$_5$, JCPDS 42-0551); Y – calcium silicate (CaSiO$_3$, JCPDS 45-0156); Z – calcium magnesium aluminium oxide silicate (Ca$_5$MgAl$_2$Si$_6$O$_{18}$, JCPDS 13-0272) and the d spacing (Å) of the peaks associated with various unknown phases are also highlighted.)
Figure 9.21: XRD diffractograms of leached calcite with various amounts of EDTA added for an extra 10 minutes after a 24-h leaching run. (Note: C - calcite (CaCO₃); P - portlandite (Ca(OH)₂) and the dspacing (Å) of the peaks associated with various unknown phases are also highlighted.)
Figure 9.22: XRD diffractograms of MK-GGBFS binder with various amounts of EDTA (Matrices W1 to W3). (Note: G – gypsum (CaSO$_4$·2H$_2$O))
Figure 9.23: XRD diffractograms of MK-CEM binder with various amounts of EDTA (Matrices X1 to X3). (Note: F – calcium iron oxide (CaFe₄O₇, JCPDS 15-0558); G – gypsum (CaSO₄·2H₂O); P - portlandite (Ca(OH)₂); X – calcium silicate (Ca₃SiO₅, JCPDS 42-0551); Y – calcium silicate (CaSiO₃, JCPDS 45-0156); Z – calcium magnesium aluminium oxide silicate (Ca₅₄MgAl₂Si₁₆O₅₀, JCPDS 13-0272))
Figure 9.24: XRD diffractograms of MK-WOL binder with various amounts of EDTA (Matrices Y1 to Y3). (Note: W - wollastonite (CaSiO₃))
Figure 9.25: XRD diffractograms of MK-CAL binder with various amounts of EDTA (Matrices Z1 and Z2). (Note: C – calcite (CaCO₃))
Figure 9.26: XRD diffractograms of MK-Ca(OH)$_2$ binder with various amounts of EDTA (Matrices V1 and V2). (Note: P – portlandite (Ca(OH)$_2$))
Figure 9.27: SEM image of a MK-GGBFS binder (Matrix W3) at 7 Days. Identification of different phases: A – geopolymeric gel with average CaO/SiO₂ and Al₂O₃/SiO₂ ratios of 0.06 and 0.22 respectively; B – calcium rich particles with average CaO/SiO₂ and Al₂O₃/SiO₂ ratios of 0.99 and 0.21 respectively and C – scattering of calcium silicate precipitates with similar molar composition as “B”.
Figure 9.28: SEM image of a MK-CEM binder (Matrix X3) at 7 Days. Identification of different phases: A - geopolymeric gel with average CaO/SiO$_2$ and Al$_2$O$_3$/SiO$_2$ ratios of 0.07 and 0.31 respectively; B - calcium rich particles with average CaO/SiO$_2$ and Al$_2$O$_3$/SiO$_2$ ratios of 0.86 and 0.16 respectively and C - calcium silicate precipitates with average CaO/SiO$_2$ ratio of 2.85 and < 0.5mol% of aluminium.
Figure 9.29: SEM images of a MK-WOL binder (Matrix Y3) at 7 Days. Figure 9.29II shows the enlarged view of Area “X” as shown in Figure 9.29I.

Identification of different phases: A – partially reacted wollastonite; B – sodium aluminosilicate phase with an average Al₂O₃/SiO₂ ratio of 0.28 and <0.5mol% of Ca; C – geopolymeric gel with an average Al₂O₃/SiO₂ ratio of 0.22 and <2mol% of Ca and D – scattering of bright white coloured precipitates that contains >8mol% of Ca.
Chapter 10

Conclusions and Recommendations

The thesis confirms previous findings that the moderate addition of a calcium material will be beneficial to the compressive strength of a geopolymeric binder and it presents new microscopic data that describes the microstructural characteristics of geopolymers containing calcium materials. In addition, the thesis represents a first attempt at relating and distinguishing the chemistry between geopolymers and ordinary Portland cement (OPC). Furthermore, the thesis has made a significant contribution to the mechanistic understanding of geopolymerisation by proposing a chemical mechanism to describe the coexistence of a geopolymer phase and calcium silicate hydrate (CSH - a major binding phase in OPC) phase in the same system. This particular result is of major significance because it aids in the explanation of durability of geopolymeric material.

The role of calcium in geopolymerisation is found to be varied, and in general, it depends on (1) the type and nature of calcium material used, (2) the alkalinity of the alkaline activator and (3) the mass ratio between different raw materials used in the synthesis. These factors all affect the concentration of “free” soluble species (most importantly silicate, aluminate and calcium) present in the alkaline medium, which will further determine the subsequent reactions that take place and ultimately the role of calcium in geopolymerisation at a specific condition. The term “free” is emphasised in the discussion because, despite being soluble, species could still be bound or “locked” with other species, such as with the complexation agent EDTA. This will inhibit the calcium to participate further in any reaction in the alkaline medium.

Improved compressive strength of the resultant geopolymer binder is generally found in binders consisting of both CSH and geopolymeric phases. CSH gel formed in such system is found to have a significantly lower Ca/Si ratio than the CSH commonly
formed from the hydration of ordinary Portland cement, while the geopolymeric gel formed is found to have similar aluminosilicate structure as the one formed in the absence of any calcium source. It is suggested in the thesis that voids and pores within the geopolymeric binder become filled with the CSH gel, which helps to bridge the gap between the different hydrated phases and unreacted particles. The result is an increase in compressive strength with time, similar to ancient concrete, which is renowned for its durability. These findings are therefore of great scientific and commercial value as they start to address the fundamental reasons for geopolymers possessing excellent durability characteristics.

The coexistence of these two phases in a single system occurs at specific conditions and it often takes place at a low concentration of NaOH and when a calcium source that can readily dissociate calcium species into the solution or gel phase (e.g. ground granulated blast furnace slag, GGBFS) is used. Calcium dissolved from a calcium source will react with soluble silicate or aluminate species in forming CSH or calcium aluminate hydrate in preference to the formation of geopolymers where calcium would play a charge-balancing role.

In cases where calcium sources have limited solubility in an alkaline solution (e.g. wollastonite and calcite), the chemical role of these materials in geopolymerisation is shown to be only minor, with insufficient amount of CSH phase forming in the system. Subsequently, a comparatively low early compressive strength (<20MPa at 28 days) is exhibited by these binders. On the contrary, the compressive strength of these binders is found to improve significantly with time. These calcium materials with low solubility play a predominant role as a physical filler/micro-aggregate in reinforcing the physical structure. The surface properties (e.g. surface structure, elemental composition) of the different calcium micro-aggregates have a vital influence over their interfacial bonding with the geopolymer. For example, the carbonate on the surface of the calcite or dolomite is likely to constitute a preferential substrate for geopolymerisation (in replacing some of the molecular and/or hydroxyl group), which will ultimately increase the compressive strength of the resultant matrix with time as demonstrated.
In a high concentration of NaOH (molarity >7.5M), the geopolymeric structure is found to be the dominant phase formed with a scattering of small calcium precipitates situated in the binder. The formation of CSH is not readily observed in this system. Calcium is found to play less of a role in affecting the nature of the end product in general, thus the extent of dissolution of calcium species from the different calcium silicate sources will not have a major impact on the resultant strength of the matrices. Subsequently, the compressive strength of the matrices synthesised at high alkalinity is found to be similar, irrespective of the type of calcium material investigated.

The coexistence of the geopolymer and CSH phases is not observed at high alkalinity unless a significant amount of “free” soluble calcium species is present initially. This can be achieved by using a calcium material that is highly soluble at high alkalinity (e.g. calcium sulphate hemihydrate) or by adding the calcium material in a substantial amount as shown in the thesis. However, due to the excessive amount of hydroxide ions present in the binder, the resultant compressive strength does not increase in the same way as that observed at lower alkalinity, even though the coexistence of both geopolymeric and CSH phases is possible.

Moreover, the presence of soluble sulphate ions in the geopolymeric system is found to promote the formation of crystalline CSH instead of the amorphous CSH, which is commonly found in the geopolymeric system in the presence of calcium silicate and calcium hydroxide. Further analysis has indicated that possible sulphate attack (in the presence of dissolved calcium species) will enhance the compressive strength of geopolymers, by initiating the formation of crystalline CSH in a geopolymeric product. This has also demonstrated the complexity of the chemistry involved in geopolymerisation with the presence of foreign ions being likely to initiate a number of reactions. Ultimately, the mechanistic path of the system is dependent on the concentration and stability of all soluble species present in alkaline media initially.

The importance of the dissolution step in determining the concentration and stability of all soluble species, thereby the mechanistic path in geopolymerisation, cannot be over-emphasised. The concentration of soluble Ca species leached from different calcium materials increases upon the addition of EDTA (i.e. a chelating agent). This appears to promote the formation of precipitates with a higher concentration of
calcium and silicon in a highly alkaline environment to some extent. However, the nucleation growth of calcium silicate hydrate (CSH) gel along with a geopolymeric phase is not promoted or observed. Rather, a large proportion of Ca species dissociated from calcium sources will form metal complexes with EDTA instantaneously. This has provided further evidence to support the proposed chemical mechanism that the formation of both geopolymer and CSH phases would only be promoted in the presence of high concentrations of “free” soluble Ca species.

Despite reaching the conclusion of the thesis, the understanding of the role of calcium in geopolymerisation is by no means “completed.” The focus of the thesis has been in the region between cement and geopolymers; the understanding of the relationship between geopolymers and Ca-zeolites through the role of calcium in geopolymerisation may open up yet another research interest. The concentrations of soluble silicate and water present in the alkaline activator, and the temperature used in the initial curing were set as constant throughout the thesis. These factors are likely to have an influence on the kinetics of the system, thus the role of calcium in geopolymerisation. In fact, simply by changing the synthesis condition of the current system (e.g. by adding more water) the formation of a Ca-zeolite along with a geopolymer phase, instead of CSH, may be affected. The possibility of a geopolymer gel consisting merely of an agglomerate of nano-crystalline zeolite phase also needs to be considered in future research.

In addition, even though it has been demonstrated that the compressive strength of binders consisting of moderate addition of calcium materials may improve with time, further testing on its acid resistance and fire resistance should be conducted in confirming its durability in an adverse environment. Also, the possible use of a ternary system (e.g. an alkaline activated system consists of GGBFS, MK and limestone) in industrial application may improve and modify the existing properties of a binary binder.

With the development of advanced analytical techniques, especially those that enable the examination of specimens in situ (e.g. synchrotron and ESEM), the understanding and the application of geopolymer technology will increase significantly. The ability to quantify the phase composition (e.g. geopolymer and CSH phase) of the resultant
binder may assist in constructing a new material with specific desired properties. This can be achieved by modelling the phase composition of the end product (e.g. different proportion of geopolymer and CSH phases) through the use of a carefully formulated recipe or mix-design (e.g. raw materials, synthesis conditions). An established method to quantify the phase composition of a geopolymeric product (especially the ratio between geopolymer and CSH phases) is not available at present. However, this study has already demonstrated for the first time that CSH phase is one of the products formed at specific conditions. The application of a selective chemical extraction commonly used in cementitious systems (e.g. Takashima's attack (salicylic acid-methanol solution), KOH-sugar solution or EDTA-triethanolamine solution) followed by a quantitative XRD analysis may represent one of the quantitative techniques used in future. The thesis has indeed established the foundation for further research in years to come.
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